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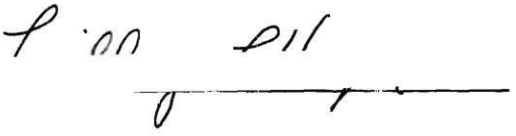

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AN ISOTHERMAL HEAT OF DILUTION CALORIMETER: THE HEAT OF DILUTION OF POTASSIUM NITRITE

A THESIS

Presented to

The Faculty of the Graduate Division

by

Fielding Ficklen Harper

In Partial Fulfillment

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Doctor of Philosophy

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AN ISOTHERMAL HEAT OF DILUTION CALORIMETER:
THE HEAT OF DILUTION OF POTASSIUM NITRITE

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Mr. Malcolm E. Rucker did much of the machine work, and acted as a helpful consultant on all steps of the design and construction of the calorimeter.

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SUMMARY

The purpose of the work reported in this thesis may be summarized in the four objectives listed below.

1. To design and build a solution calorimeter which would be fast and convenient to use.

2. To write and check out computer programs to reduce the data from the calorimeter.

3. To demonstrate the usefulness of the system by measuring the enthalpy of dilution of potassium nitrite.

4. To leave an operating system for future use, by anyone, without the necessity of extensive training.

Partial success was achieved on three out of the four goals, but one goal had to be abandoned.

The calorimeter was built. In use it proved to be fast. All the data for KNO_2 were collected in four weeks, in contrast to the traditional twelve to eighteen months. The enthalpies derived from these data are presented in tabular and graphical form. Unfortunately, the data were not as precise as desired due to an unfavorable laboratory environment. Calculations indicate that at least an order of magnitude improvement in the precision would be expected in a better environment.

Three major programs were written. These reduce the raw data from the calorimeter to ΔQ's, calculate the relative apparent molal enthalpy from the measured ΔQ's and solution concentrations,

and perform nonlinear curve fitting. In addition, a number of small service type programs were written. The major programs worked well, both on the data from the calorimeter described in this thesis and on data from other sources.

Usefulness of the system could not be clearly demonstrated due to the poor precision achieved. The lack of precision was particularly apparent in the low concentration region, where data are needed for extrapolation to the infinitely dilute standard state. Only one point was measured below 0.1 M, and only five below 0.5 M. These were not sufficient to allow the extrapolation. Even for these five points the measured energy change was of the same order of magnitude as the uncertainty.

The system was not left in operating condition because of demands on the laboratory space which it occupied. Since no one has indicated an immediate interest in using the calorimeter, the space was released to other workers.

The final design of the calorimeter consisted of an isothermal, phase change type of solution calorimeter. This design was chosen for several reasons. The true isothermal nature of the calorimeter reduces the number of experimental data that must be collected. Also, the interpretation of the data is more straightforward, as no corrections must be applied to the observed data.

In addition to reducing the experimental work, the design of the calorimeter simplified construction. As the temperature was fixed, there was no need to minimize the heat capacity, and therefore mass, of the calorimeter. It was possible to make the calorimeter

mechanically strong, with a resulting ease of fabrication.

Another advantage of the isothermal phase change type of calorimeter is that it does not require extensive instrumentation for operation. The only instruments required are a balance, a temperature regulator, and a vacuum gauge.

Diphenyl ether was chosen as the working medium of the calorimeter because of its convenient melting point (26.9°c), chemical stability, and known properties. However, it was necessary to purify the diphenyl ether by several physical means.

Several recommendations are given for future users of this calorimetric system or similar systems. It is hoped that these recommendations would lead to better performance from the system.

CHAPTER I

INTRODUCTION

Physical chemists and physicists are interested in the fundamental laws of nature so that they may make predictions of the behavior of matter in situations which have not been subjected to experimental investigation. One general approach to elucidating these laws is by means of mathematical models which approximate real systems.

Gases have been treated in this manner, and the Kinetic Theory of Gases is the result. The original mathematical model was of elastic, point masses obeying classical laws of motion.

In a similar manner, theories of ionic solids have been developed based on point charges on lattice sites interacting according to Coulomb's laws. Naturally there have been extensive additions to the original theories.

When one tries to deal with liquids, the situation is not as clear. As yet there are no completely satisfactory theories of liquid behavior. Moelwyn-Hughes[1] gives a picturesque description of liquids.

> The liquid state of matter is thus an intermediate one. Like a central party in politics or a moderate denomination in religion, it is less rigorously defined and more difficult to understand than either of the extremes that flank it.

Even less well defined are solutions. Added to the imprecision of knowledge of the liquid state are the various interactions between the solute and the solvent.

Despite the generally gloomy picture of solution theory, there

are theories which describe certain types of solutions reasonably well. The classical example is the Debye-Hückel[2] theory of electrolyte solutions.

In general terms there are two types of effects that must be considered by any theory of electrolyte solutions. These are the ideal mixing effects, and the non-ideal mixing effects. The ideal mixing effects are those associated with mixing two substances to give a solution which is ideal from the thermodynamic point of view.

The non-ideal effects are those which give rise to departures from ideal behavior. In the case of solutions of electrolytes the non-ideal effects are generally attributed to ion-ion interactions, to ion-solvent interactions, and to minor effects due to modifications of solvent properties by the fields associated with ions.

For practical reasons only ion-ion interactions are usually considered. The ion-ion interactions are electrostatic in nature and involve much stronger forces than ion-solvent interactions. While it would be desirable to have a theory which would include the ion-solvent and other interactions, practical necessity dictates that only ion-ion interactions be considered.

Debye and Hückel[2] formulated a theory which considers ion-ion interactions at relatively long distances. That is, their theory treats dilute solutions. Interested readers are referred to Debye and Hückel's original paper for details, or to the translation which appears in The Collected Papers of Peter J. W. Debye. There are several points which should be mentioned regarding the Debye-Hückel theory. As mentioned, it is concerned with ion-ion interactions is dilute solutions. The restriction to dilute solutions is inherent in several of the assumptions made

in the development of the theory. The major assumption is that the only electrostatic interaction between ions is between charged spheres in a uniform medium. Specifically, "contact" between charged spheres is not considered. In fact, a fairly large distance between ions is implicit in the assumption that the solvent is a uniform medium. That is to say, the distance between ions must be large enough so that the molecular structure of the solvent is "averaged out." These assumptions are valid only at extreme dilution, if at all.

Mathematical approximations also limit the Debye-Hückel theory to low concentrations. The theory involves the potential experienced by an ion in a field. The field is described by the Boltzmann-Poisson equation, which has the form of an exponential. In order to express the electrical free energy of an ion, it is necessary to solve a second order differential equation involving this potential and appropriate boundary conditions. This equation does not admit to a solution. Therefore, Debye and Hückel expanded the exponential in a series, and discarded all but the first term. This approximation is valid only under conditions when the ions are widely separated, that is at high dilutions.

The Debye-Hückel theory is usually used to obtain the activity coefficient of the electrolyte in dilute solutions. However, Debye and Hückel used the theory to calculate what they called the electrical free energy.

By application of the Gibbs-Helmholtz equation to the electrical free energy, ΔG_{el}, one obtains an expression for the electrical enthalpy, ΔH_{el}, of the solution.

$$\Delta H_{el} = -T^2 \frac{\partial(\Delta G_{el}/T)}{\partial T}$$

where T is the absolute temperature.

Here the electrical enthalpy, ΔH_{el}, is equal to the apparent molal enthalpy referred to the "infinite dilute" state. Using the notation of Lewis and Randall[3] this is:

$$\Delta H_{el} = \phi_{H^\circ} - \phi_{H^\circ} = \phi_L$$

Since 1923, much of the experimental work in the field of electrolyte solutions has been aimed at testing the Debye-Hückel theory. For example, see Lang and Robinson.[4] If consideration is limited to dilute solutions where the Debye-Hückel theory is expected to be valid, the theory has been confirmed by all experimental tests. In fact, the Debye-Hückel theory can be safely accepted as "proved" by experiments. Thus, the Debye-Hückel theory can be used as a guide for extrapolation of experimental data to the "infinitely dilute" state.

With this background of theory supported by experiment, it would be hoped that large amounts of experimental data would be available for use in thermodynamic calculations. Unfortunately, this is not the case.

A major deterrent to the collection of data has been the time needed to collect and to reduce the data to usable form. Two general approaches are available. The first is to determine the activity of the electrolyte as a function of concentration over a range of temperatures. By straightforward application of thermodynamics, the enthalpy of dilution can then be obtained. The limiting factors here are the need to make a

large number of measurements and to insure that they are highly precise.

The second approach is to measure the enthalpy of dilution -- generally called the heat of dilution -- as a function of concentration directly in a calorimeter. This can be done at some convenient temperature. Attractive as this approach seems at first sight, the experiments are not easy to perform.

The calorimeters used in previous work have been of a number of designs. One feature which they all seem to have in common is that they are inconvenient to operate. Added to the difficulties of determining the enthalpy of dilution is the involved data reduction which is necessary. Lang and Robinson[4] describe a typical calorimeter, and indicate some of the time consuming features it exhibits. Sunner and Wadso[5] undertook the design of a solution calorimeter of a more or less conventional design. Their paper should be consulted for some of the problems in calorimeter design. Although most papers do not indicate how much time is required to make a series of runs, it is possible to infer that eighteen to thirty-six months are required to determine all of the data necessary to define the enthalpy of dilution of one salt. This does not include the time necessary for constructing the calorimeter. Thus, it is not surprising that not many salts have been investigated.

With this as a background it is now possible to define the goals of the project reported on in this thesis. There were four goals. 1. To design and build a calorimeter which would be fast and convenient to use. 2. To write and check out computer programs to reduce the data from the calorimeter. 3. To demonstrate the system by measuring the

enthalpy of dilution of KNO_2. 4. To leave an operating "system" so that more work could be done in the future.

It was hoped that if such a system were available, graduate students would undertake enthalpy of dilution studies in connection with other more extensive research projects.

This thesis will describe the steps taken to accomplish the above goals. However, it should be stated that these goals were not completely met. The calorimeter was constructed according to designs dictated by the above considerations, and the necessary programs were written. Unfortunately, the calorimeter did not perform as well as desired due to an unfavorable laboratory environment. In its present form, the calorimeter is capable of yielding useful results in a more stable environment. However, as it was not possible to provide a better environment at this time, the results of this project are not conclusive. Nevertheless, the calorimeter should serve as a prototype for other investigations.

CHAPTER II

CALORIMETER SYSTEM DESIGN PHILOSOPHY

The lack of heat of dilution and heat of solution data in the past may be due in large part to the experimental difficulties in making such measurements. The calorimeters used were usually of the so-called mixing type, where the energy effect to be observed was converted into a change of temperature, which was then measured.

A number of difficulties arise from this method. In the first place, several measurements had to be made in order to get one value. These would involve measuring the "heat equivalent" of the reactants in the calorimeter before mixing, and also the "heat equivalent" of the system after mixing. Thus up to three separate runs were required to get one value. Of course, many of the calorimeters used were so designed that the "after heat equivalent" from one dilution also served as the "fore heat equivalent" of the next dilution. Nevertheless, physical limitations restricted the number of dilutions which could be conducted in series.

In converting the energy change of interest into a change in temperature the need for very precise temperature measurements arises. Of course what is measured is differences in temperatures rather than absolute temperature. However, this still presents problems. The most common methods of measuring temperature changes before the advent of thermistors were resistance thermometers and thermopiles. Resistance

thermometers were generally used in single vessel calorimeters, while the thermopiles were usually employed in the twin vessel calorimeters, generally called Joule twin calorimeters. Either type of measurement gave rise to its own peculiar problems. If a resistance thermometer was used one was faced with the choice of using a commercially available coil with some difficulties in thermally coupling the coil to the calorimeter, or winding the coil in the laboratory. The latter expedient was usually chosen, however there were still problems associated with ensuring an unstrained coil, and indeed in uneven temperature distribution over the outer surface of the calorimeter. For example Gunn[6] found that when he measured the heat of solution of KCl a "cold spot" formed on the bottom of the calorimeter, presumably due to the solid KCl settling to the bottom before being dissolved.

Another difficulty with both resistance thermometers and thermopiles is the matter of calibration. One either has to accept literature values or make some attempt to calibrate the thermometer as installed. This often involves things like establishing "fixed points" e.g., the ice point, and assuming a specific response between the fixed points.

More recent calorimeters have used thermistors to detect changes in temperature. For example Swanson[7] describes a calorimeter using two thermistors in series. Due to the much smaller mass of the thermistors as compared thermopiles or resistance units, the thermistor shows a more rapid response. Also, in general the thermistor shows a greater change in properties with temperature than either of the other systems. This means that it is more sensitive to small changes in temperature. By using a small temperature change some other undesirable

effects of temperature change calorimeters are minimized.

No matter what device is used to measure the change in temperature in such a calorimeter, it is necessary to measure the "energy equivalent" of the calorimeter. The usual technique for doing this is to include an electrical heater in the calorimeter. Before a run a known amount of electrical energy is put into the heater and the resulting temperature change in the calorimeter measured. One has to exercise care in using the heater, so that the energy change is of the same order of magnitude as that expected from the reaction of interest. The measurement of the quantity of electrical energy introduced into the calorimeter through the heater involves the careful measurement of current, voltage, and time. These requirements usually result in the use of rather sophisticated equipment.

In addition to the experimental difficulties mentioned above, data reduction is a time consuming process. The output from each dilution experiment, and from each calibration is either a series of time-temperature points or a time-temperature curve from a recorder. This has to be manually converted to a temperature change, and that converted to an energy change through use of calibration data. Once the energy change for a given dilution is known relative partial molal enthalpies for one solution can be calculated if that of the other two solutions involved are known. If two enthalpies are not known, one or both must be obtained by interpolation on a large scale graph of $^{\varphi}L$, the relative partial molal enthalpy, against the square root of the concentration. In this manner a series of $^{\varphi}L$-concentration points is obtained.

There are several disadvantages to this method of data reduction.

In the first place it is time-consuming. As much time is required in reducing the data as in collecting the data. In the second place some of the precision of the data is inevitably lost in the graphical manipulation. And in the third place the process becomes somewhat subjective.

The major aim of the research reported in this thesis was to produce a calorimeter system which would overcome as many as possible of the objections listed above, and which would be designed so that rapid collection of the required data would be the normal mode of operation.

To achieve this aim a number of design features were adopted. By making the calorimeter truly isothermal, it is possible to eliminate several of the objectionable features of the older calorimeters. Since there is no temperature change, there is no need to determine the "heat equivalent" of the calorimeter before and after each experiment. In addition to reducing the amount of experimental data that has to be collected this step eliminates the need for the elaborate equipment needed to measure the electrical energy put into the calorimeter.

The method of making the calorimeter isothermal was to employ a mixture of solid and liquid diphenyl ether as an energy reservoir. The diphenyl ether was thoroughly purified, and, since only a very small portion of the total charge changed phase in any run, it can be said that the reaction is isothermal. In addition to eliminating the need for the extra "calibration" runs, the process of data collection was speeded up by the design of the calorimeter. The ideal which was aimed for was to make it possible to complete one dilution and be immediately ready to start the next. This ideal was not achieved, but still it proved

possible to make a dilution run every sixty to ninety minutes.

The next logical step in simplifying and speeding up the process of obtaining heat of dilution data was to employ the computational abilities of high speed digital computers in the data reduction. Thus, a very important part of the calorimeter system consists of the computer programs which reduce the data to useful form. Again the ideal was not achieved, as it is necessary for the experimenter to manually intervene, but most of the computation and decision making is taken over by the program package.

One great advantage obtained from the choice of calorimeter design was in the field of instrumentation for control and observation of the environment of the calorimeter. In contrast to the racks of "electronics" usually associated with a precision calorimeter, the calorimeter described in this thesis required only a thermostat (home made) and a vacuum system for operation. Admittedly, the performance would have been better if more precise control over the temperature of the room and the thermostat could have been exercised.

CHAPTER III

CALORIMETER SUBSYSTEM

The design philosophy given above dictated the design of the calorimeter itself. However, additional constraints were placed on the design by the availability of materials and of fabrication techniques. Thus, the shape of the reaction vessel of the calorimeter was fixed by the availability of 6 inch diameter aluminum rod and by the requirement that it should contain about one liter of solution. Similar considerations dictated the design of other components of the calorimeter.

Because of the isothermal nature of the calorimeter design, it was possible to construct the components on a more massive scale than is usual in calorimeter construction. In the conventional design the heat capacity of the calorimeter must be kept to a minimum in order to provide as large a change in temperature for a given energy input as possible. This requirement in turn dictates that the mass of the calorimeter be kept to a minimum. In contrast, the phase change type of calorimeter, the temperature is fixed at the melting point of the working medium, and therefore the heat capacity of calorimeter components is immaterial. In fact, the requirement that the volume of the diphenyl ether chamber be fixed demands mechanical rigidity, indicating the use of massive components for mechanical strength.

As finally constructed, the calorimeter consists of a series of coaxial vessels. Listed from the outside inwards, the vessels are a

vacuum jacket, the diphenyl ether chamber, the reaction vessel, and the pipette.

The distinguishing feature of the calorimeter is the ability to manipulate the stoppers of the pipette from outside of the calorimeter proper, and the facility with which the pipette and the reaction vessel can be filled or emptied. The filling operations can be performed without dismantling any part of the calorimeter, and the control for opening the pipette is constructed so that it may be opened, by lifting a collar above the drive sprocket, without interrupting the stirring of the contents. These two features contribute to the rapid collection of data since it is possible, and indeed is the planned mode of operation, to make a series of "runs" by emptying the pipette at the end of one run, and then immediately refilling it and starting the next run.

Calorimeter Design Details

Applying the design philosophy outlined in Chapter II to the actual design of the calorimeter necessitated a number of compromises. The calorimeter was constructed out of aluminum with the exception of certain bearings and tubes. However, in order to present an inert surface to the solutions undergoing test all surfaces which could contact the solutions were coated with Teflon, made of Teflon, or, in the case of inlet and outlet tubes, made of type 316 stainless steel.

Materials for Teflon coating aluminum were kindly supplied by Dr. W. Mosely and Dr. R. LeBlue of duPont. The instructions which came with the materials were designed to assist in coating cooking ware, and

were not directly applicable to the more complex shapes of the calorimeter parts. Therefore a development program had to be undertaken to devise methods of applying the Teflon. These finally proved successful, with one exception. It was not possible to obtain a continuous coating on the inside of small diameter aluminum tubing. For this reason, type 316 stainless stell was substituted for the aluminum in the tubing. The stainless steel tubing is part of the removable portion of the calorimeter, and thus easy to inspect for corrosion. It would not be difficult to replace the stainless steel tubing if it deteriorated.

Since it was essential that the volumes of the various chambers remain constant over the life of the calorimeter, and that gooc mechanical seals with no crevices be provided, most of the joints were welded. Later experience showed that it would have been possible to use gasketed joints, using Teflon as gasket material. The welded design gave rise to a number of problems. It was necessary to coat some of the parts with Teflon before the welding was complete. This in turn made it necessary to protect the Teflon coating from excessive heat during the welding. (Teflon coating decomposes above 400°C). Thus some of the parts were designed so that they could be filled with water during the welding of adjacent joints.

The final design of the calorimeter consisted of a series of coaxial cylinders. From the inside out these cylinders or chambers are called the pipette, the reaction vessel, the diphenyl ether chamber, and the vacuum jacket.

The pipette (A in Figure 1, also A in Figure 2) is contained within the stirrer, and therefore rotates with the stirrer. It consists

of a chamber of 84.03 $\pm$ 0.05 cm^3 volume. At the beginning of a run the pipette was sealed at the top and bottom with tapered plugs. These plugs are connected in such a way that they may be opened while the stirrer is rotating, thus initiating the mixing of the solutions in the pipette and the reaction vessel. It is possible to fill or empty the pipette through a 1/4 in. stainless steel tube, which extends to the top of the calorimeter. The volume of the pipette is fixed by an overflow, arranged so that the hydrostatic heads on both the pipette and the reaction vessel are approximately equal.

The stirrer (B in Figure 1) is designed so that it will impart several different types of motion to the solution. The stirrer is shown in Figure 2, and a photograph of it included in Figure 3. The lower section of the stirrer is a turbine stirrer which will force solution from the centerline toward the outer wall of the reaction vessel. (B in Figure 2, also shown in cross section in Figure 2.) The opening of the pipette is just above this section of the stirrer, and on the center line. When the pipette is opened the solution in it (if it is denser than that in the reaction vessel) tends to settle into the center of the turbine. Here the solution is thrown to the outside of the reaction vessel after undergoing shearing type mixing in the turbine blades. In practice it was found that the mixing time for a lighter solution in the pipette was in the order of three times as great as the mixing time when the more dense solution was in the pipette.

Above the turbine section of the stirrer is an Archimedes' screw designed to raise the denser solution from the bottom of the reaction

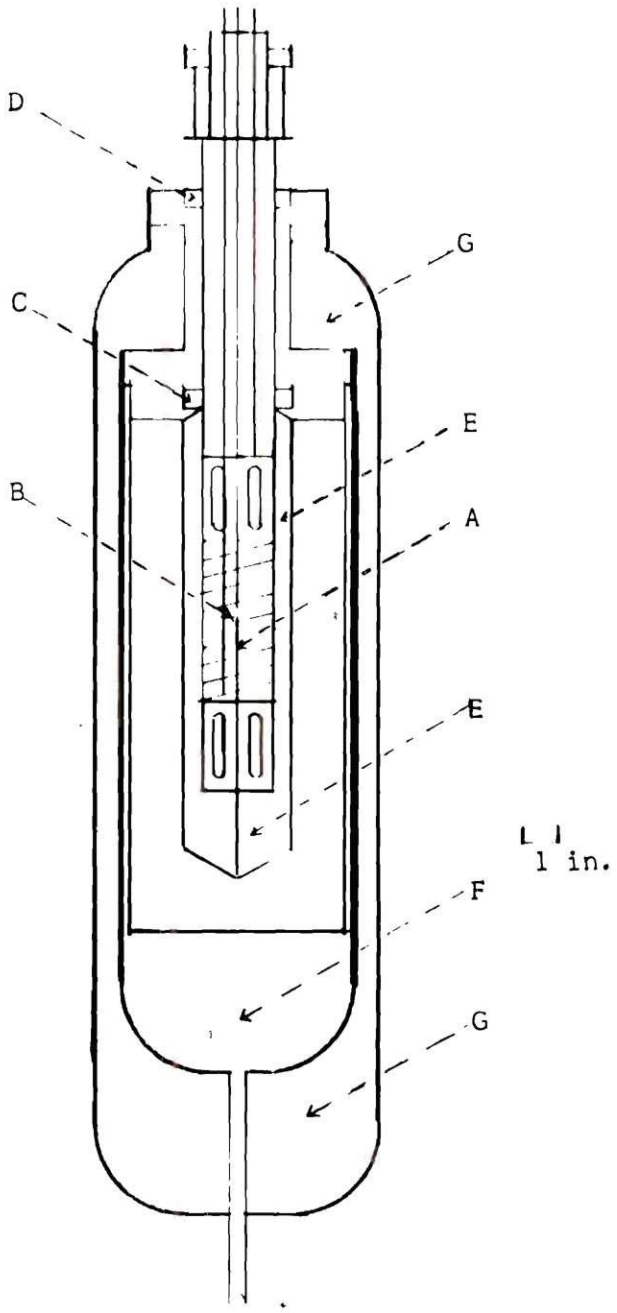

Figure 1. Cross Section of Calorimeter.

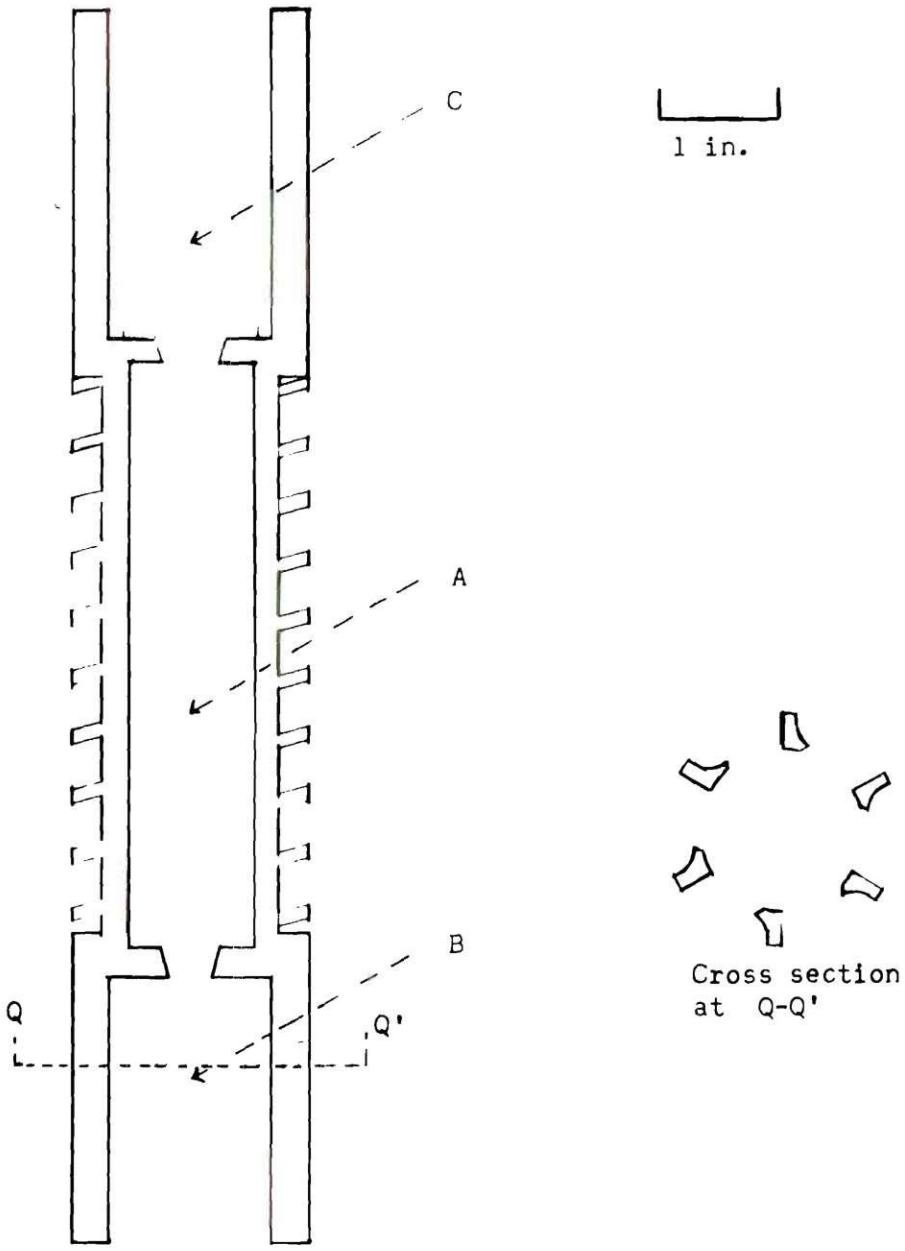

Figure 2. Detail of Stirrer.

vessel to the top, and thus to promote mixing.

The top section of the stirrer is an open cage (C in Figure 2). When the pipette is open the solution circulates through insuring thorough mixing.

The stirrer is supported by a Teflon sleeve bearing (C in Figure 1), which also forms the top seal of the reaction vessel. At the top of the calorimeter the stirring assembly is supported by a precision ball bearing (D in Figure 2). Also at the top of the calorimeter is a sprocket for the chain drive to the stirrer. The stirrer is driven at 200 rpm.

Surrounding the stirrer is the reaction vessel (E in Figure 1). This is more or less a cylinder. The top and bottom of the cylinder are conical so that no bubbles will be trapped when the reaction vessel is filled and so that all of the solution may be drained through a 1/4 in. stainless steel tube, which extends down through the stirrer from the top of the calorimeter. The volume of the reaction vessel with the stirrer in place is 1071.6 $\pm$ 0.3 cm^3. The top of the reaction vessel is defined by an overflow into the stirrer assembly. This is the same place that the overflow from the pipette discharges, and it is arranged so that it may be kept dry by applying suction to a tube that extends from it to the top of the calorimeter.

The reaction vessel was machined from a piece of 6 in. aluminum rod. The inner diameter is about 3 in. with most of the remaining wall thickness taken up with fins which were machined on the outside of the rod. These fins extend into the diphenyl ether chamber. They serve both to support the mantle of solid diphenyl ether, and to conduct

energy into or away from the reaction vessel. A disadvantage of using diphenyl ether as a working medium in this type of calorimeter is that diphenyl ether is a very poor heat transfer medium. Therefore, it is necessary to insure that there is a great deal of aluminum surface in contact with the diphenyl ether. The fins are 1/16 in. thick, spaced 1/16 in. apart. The finned portion of the diphenyl ether chamber extends from just below the Teflon bearing to over an inch below the bottom of the reaction vessel. At the top of the diphenyl ether chamber, there is a section of aluminum metal about 1 in. thick which acts as a heat sink for the bearing, conducting the energy liberated in the bearing into the diphenyl ether. The top bearing of the stirring assembly, the ball bearing, is isolated from the diphenyl ether chamber by a 5 in. cylinder of aluminum 3 in. in diameter, with a wall thickness of 3/8 in. It would be desirable to have a longer path over thinner material from an energy leak point of view, but this piece also carries the weight of the finned cylinder, and therefore had to be mechanically strong. See Figures 3, 4, 5 for photographs of the finned cylinder before the Teflon coating was applied.

There are two openings into the diphenyl ether chamber. Centered in the bottom is a 1/2 in. aluminum tube which leads to the "plumbing" on the outside of the calorimeter proper. At the top of the chamber is another 1/2 in. aluminum tube which was used to evacuate the chamber during the filling process. It is also connected into the external plumbing through appropriate valves. The diphenyl ether chamber is F in Figure 1. A block diagram of the "plumbing" is given in Figure 6.

Surrounding the diphenyl ether chamber and extending to the top

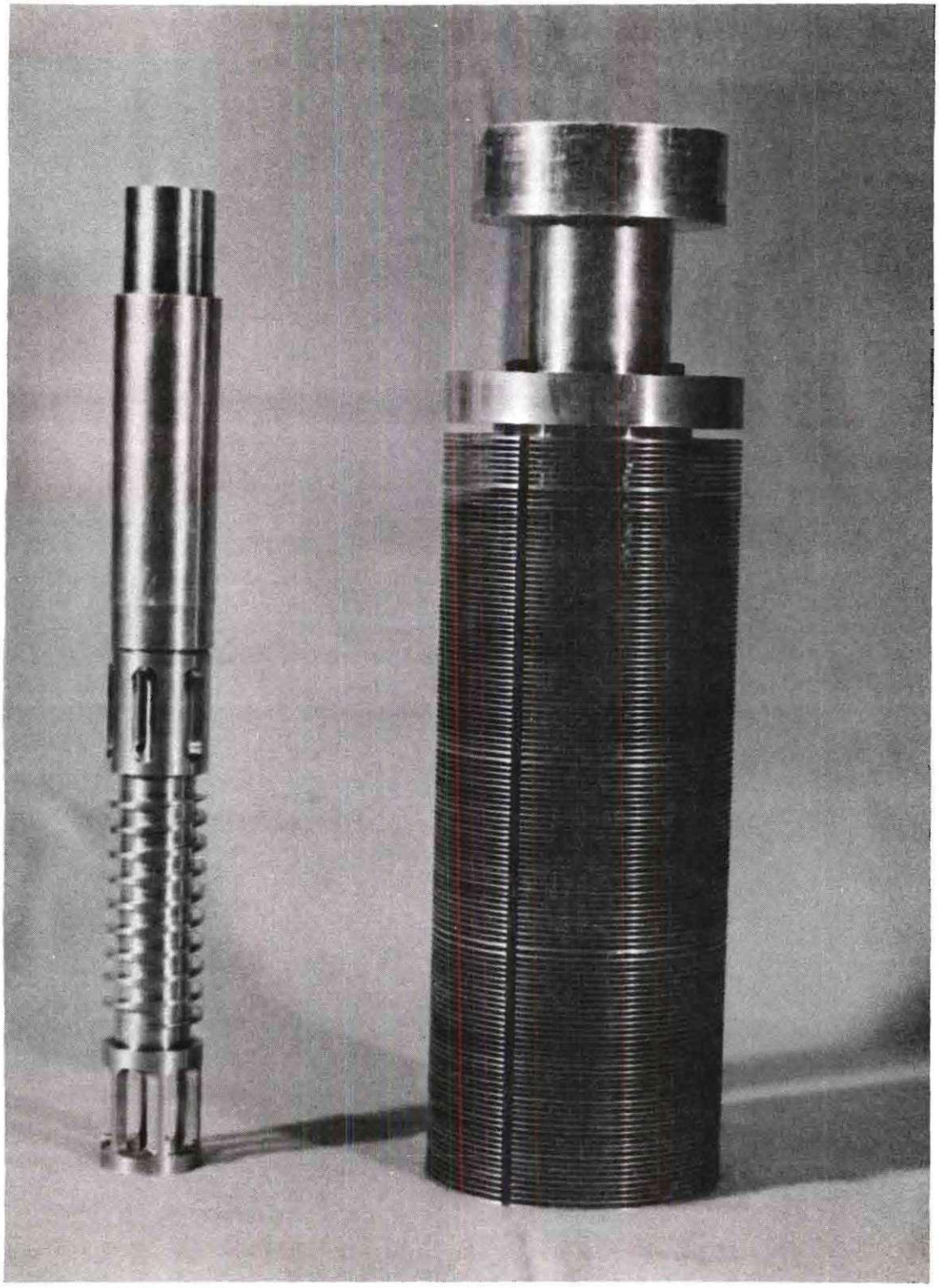

Figure 3. Stirrer Assembly (L) and Finned Cylinder (R).

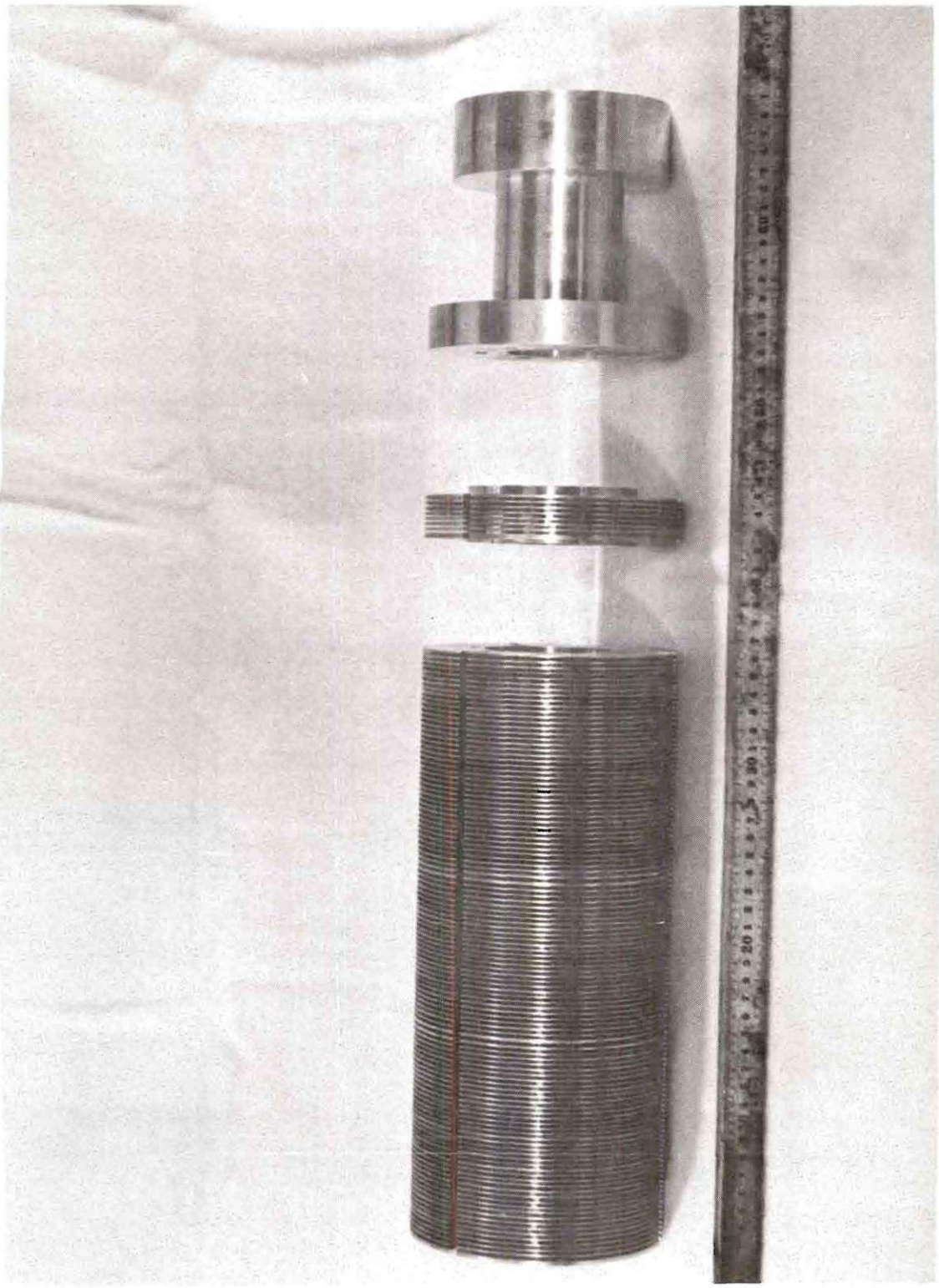

Figure 4. Finned Cylinder and Bearing Supports. Meter Stick for Size.

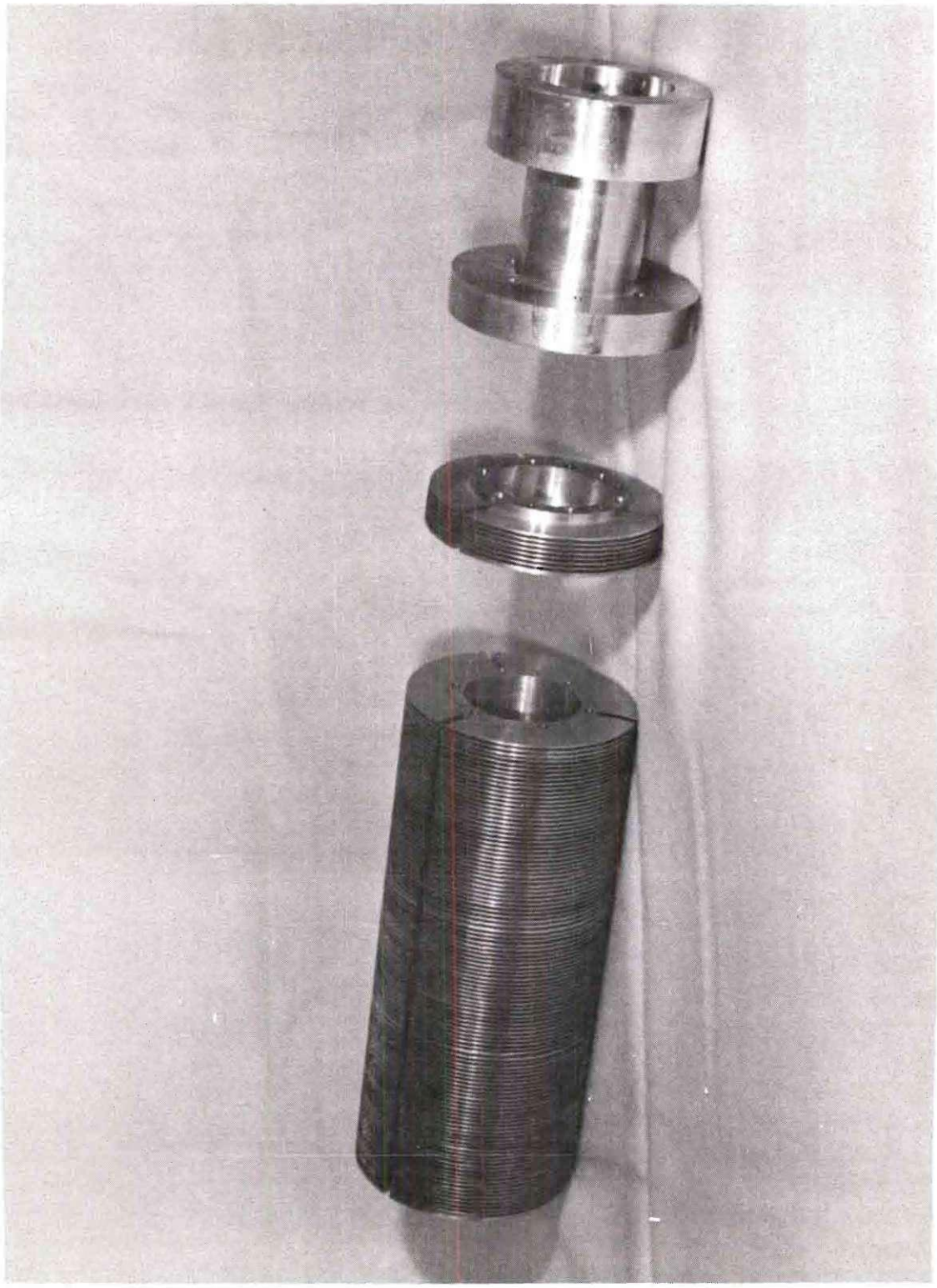

Figure 5. Finned Cylinder and Bearing Supports.

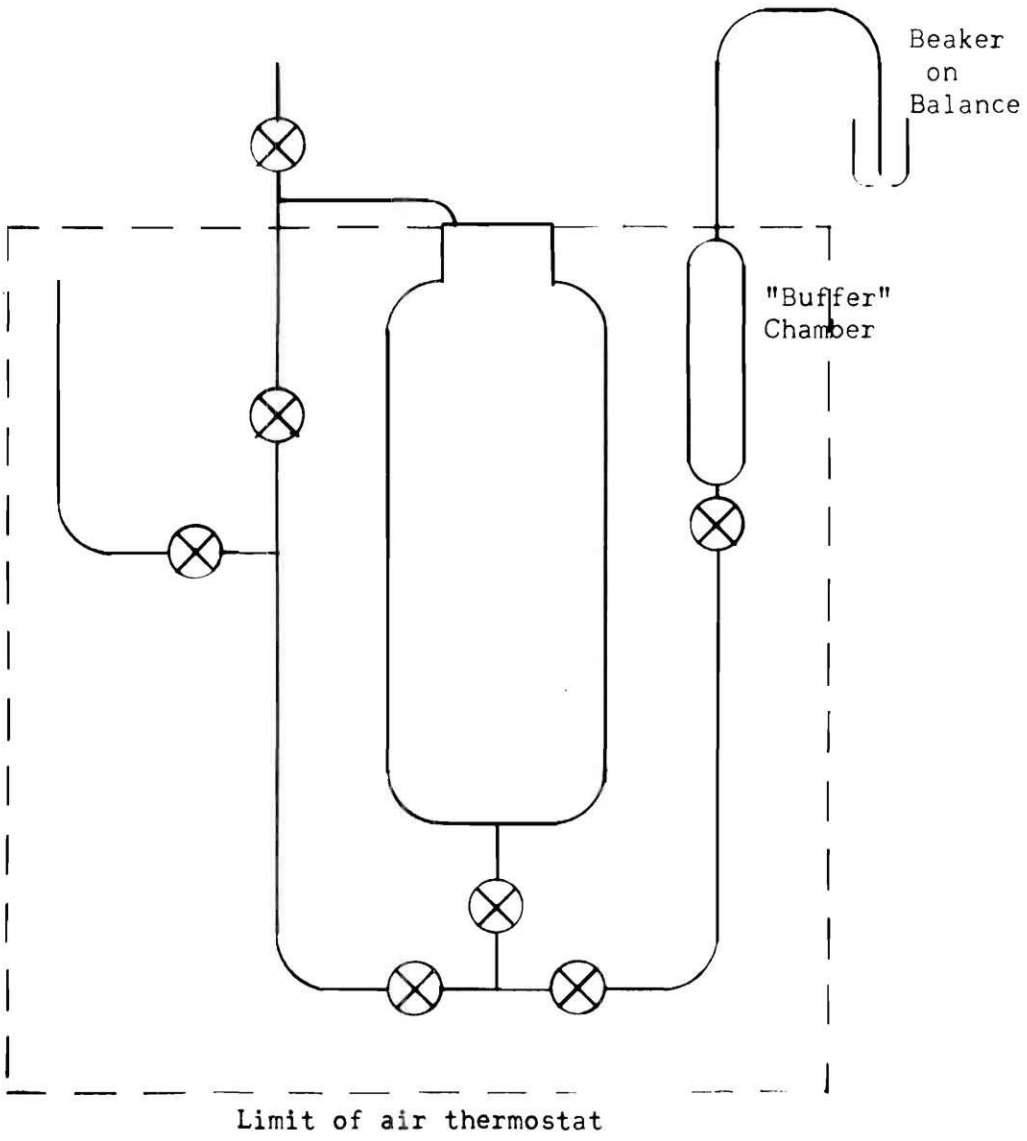

Figure 6. Block Diagram of "Plumbing."

of the calorimeter is a vacuum jacket (G in Figure 1). This consists of 8 in. aluminum pipe with end caps to seal the ends. There are openings in the vacuum jacket to allow the stirring assembly to extend into the reaction vessel, and the two tubes into the diphenyl ether chamber pass through the vacuum jacket.

All joints in the vacuum jacket, between the vacuum jacket and the diphenyl ether chamber, and between the diphenyl ether chamber and the reaction vessel were checked with a helium leak detector. The welded joints were rewelded until no leaks could be detected on the most sensitive usable scales on the leak detectors. The main joint between the reaction vessel and the bearing support was not welded, but consisted of a Teflon gasketed compression joint. It was found that this joint would not hold better than about 0.1 torr on the outside against atmospheric pressure on the inside. However, when the vacuum was helping to compress the gasket, the joint was tight. In normal operation of the calorimeter the pressure difference across this joint would be small, so this potential leak was ignored. During the filling of the diphenyl ether chamber this was not the case, and the interior of the reaction chamber had to be evacuated as well as the diphenyl ether chamber.

The entire calorimeter was mechanically rigid, so a rather simple suspension system was sufficient. This consisted of a pair of aluminum blocks with semicircular cutouts which clamped the neck of the vacuum jacket, just below the top of the calorimeter. In order to align the axis of the calorimeter with vertical an additional aluminum block supported the calorimeter at the bottom. Both the top blocks and the bottom block could be adjusted in the horizontal plane by means of screws.

The bottom block could also be adjusted vertically in order to provide a snug fit against the bottom of the calorimeter.

The plumbing associated with the calorimeter consisted of 1/2 in. and 1/4 in. aluminum tubing and type 316 stainless steel Swagelok fittings and valves. There was not much plumbing, so no attempt was made to support it separately. Instead it was suspended from the calorimeter.

The vacuum jacket of the calorimeter was constantly evacuated by a vacuum system consisting of a mercury diffusion pump backed by a mechanical vacuum pump. The major part of the vacuum system was constructed from Pyrex glass. The joint to the calorimeter vacuum jacket was by means of a standard taper joint. An aluminum outlet was welded to the vacuum jacket. This outlet was machined to conform to the dimensions of the inner member of a 24/40 $\overline{\text{S}}$ joint. An outer member of glass was fitted over this outlet, and sealed in place. At first Apiezion W wax was used to insure a good seal. However it was found that this seal leaked, and so an additional seal of Dow Ceramic Cement was applied. This seal was apparently tight.

Pressure in the vacuum system was measured by means of a Consolidated Vacuum Corporation Type 110B Ionization Gauge, with a thermocouple accessory. During the time that the calorimeter was being used to make measurements the pressure in the vacuum system was in the range of $1 - 3 \times 10^{-6}$ torr.

In addition to the standard ionization gauge it was found desirable to install several safety features in the vacuum system. These consisted of an additional 1 liter trap placed between the diffusion pump and the mechanical pump, and a manometer switch which was arranged to cut off

power to the diffusion pump if the pressure in the low vacuum side went above about 1 torr. Both of these features were found desirable to minimize loss of mercury vapor to the laboratory in the case of a break in the glass vacuum system. As the laboratory floor was rather unstable the glass vacuum system broke with distressing frequency.

To insure consistent operation of the calorimeter, it was inclosed in an air thermostat. The thermostat extended to the top of the calorimeter such that the stirrer drive chain and the controls for opening the stoppers of the pipette were outside the thermostat. The balance used to record changes in the amount of diphenyl ether in the diphenyl ether chamber was also located outside of the thermostat.

Basically the thermostat consisted of a wooden box which served to contain the constant temperature air, a blower to supply a constant amount of air to the thermostat, heaters to control the temperature of the incoming air, and a regulation system to supply power to the heaters as needed.

Three hundred cubic feet of air per minute are supplied by the blower. This volume of air is large enough that it was not necessary to insure that the thermostat box was air tight. However, most of the fixed joints were taped with masking tape to insure relatively tight seals.

The heaters consist of wire screens mounted at the outlet of the blower. Three heaters are mounted in the air stream, but it was found that the controller was not capable of supplying enough power for all three, so only two heaters were connected in parallel. The third was left as a stand-by. In practice it was found that the controller never was called on to supply full power to the heaters, at least in normal operation.

Occasionally the outside temperature would drop rapidly, and the room temperature of the laboratory would drop below 20°C. Under these conditions the controller would not be able to supply enough electrical power to maintain the thermostat at 27°C. These incidents were doubly unfortunate, since the usual result would be that too much of the diphenyl ether was frozen, and it would take 48 hours or more for the system to regain control.

Controlling the heaters was a transistor temperature regulator. The sensing element is a thermistor mounted in the air thermostat. The resistance of this thermistor controls the rate of charging of a capacitor, which in turn controls the point in the cycle at which a unijunction transistor fires. The unijunction transistor turns on a silicon controlled rectifier, used as a switch, when it fires. The SCR then conducts for the remainder of the cycle, supplying power to the heaters for part of each cycle. The basic circuit of the controller was taken from the GE Transistor Manual.[8] The circuit was modified by using a series of fixed resistors, selected by a rotatory switch, in place of a gain control potentiometer. It was found that the temperature setting as well as the sensitivity of the controller were extremely sensitive to the setting of the gain control. The combination made it impossible to establish a setting for the controller, as long as a potentiometer was used as a gain control.

Calorimeter Design Rationale

Having described the details of the calorimeter and some of the support systems, it would be in order to set forth some of the reasons behind the choices made.

The choice of an isothermal, phase change type of calorimeter was dictated by several considerations. Among others these include directness of measurement, straight forward interpretation of the results, and simplicity of mechanical construction. Using diphenyl ether as a working medium in the calorimeter was dictated by its convenient melting point, 26.9°C, by its chemical stability, by its ease of purification, and by the availability of data on it from the National Bureau of Standards. Despite these advantages, there are some drawbacks to the use of diphenyl ether. These include the fact that it absorbs air very readily, that it is a poor heat transfer medium, and that it may react chemically with mercury.

Expanding on the above mentioned considerations supports the choices made. The isothermal, phase change type of calorimeter is characterized by the directness of measurement. The effect to be measured in a solution calorimeter such as the one described in this thesis is the change in energy which occurs on mixing two solutions. In the conventional calorimeter this energy change is converted to a temperature change, and the temperature change observed by suitable instrumentation. In contrast, in a phase change calorimeter the energy change is transformed into a change in phase of some of the working medium. A measure of the extent of this phase change then can be converted back into a measure of the energy change. The measuring tools used in the current work were a balance and a clock. The balance measured the change in mass of a portion of liquid diphenyl ether. This portion of diphenyl ether is directly connected to the two phase mixture of diphenyl ether inside the calorimeter by the plumbing system

of the calorimeter. Thus there is actually a constant mass of diphenyl ether in the calorimeter and on the balance. The only change is in the amount in each location. The change in mass of the diphenyl ether on the balance pan is dependent only on the change in energy in the calorimeter, the heat of fusion of diphenyl ether, and the densities of the solid and liquid diphenyl ether. By measuring the change in mass of diphenyl ether on the balance pan with time before and after conducting the reaction of interest in the calorimeter, reliable estimates of the so-called heat leaks of the calorimeter can be made. These heat leaks include the energy transferred to the system by the stirrer and all unwanted energy transfers between the environment and the calorimeter.

The isothermal nature of the phase change calorimeter permits straight forward interpretation of the results. The solid to liquid ratio of the diphenyl ether is changed only slightly, and since the diphenyl ether is in a highly pure state, the change in temperature of the melting point of the diphenyl ether, and thus of the entire calorimeter, is very small if not zero. Typically something less than ten grams of diphenyl ether out of approximately seven and a half kileograms undergoes phase change during the course of a single run. In fact during a series of runs the typical situation was that the difference between the greatest and least mass on the balance pan was in the order of five grams.

The true isothermal nature of the phase change calorimeter completely eliminates the necessity of measuring the "heat equivalent" of the calorimeter. The saving in time is obvious, but not so obvious

is the saving in precision of the results. When it is necessary to measure the heat equivalent in connection with measuring the energy change of interest, any uncertainty in the heat equivalent causes a corresponding uncertainty in the measured energy change.

Another advantage of the true isothermal nature of the phase change calorimeter is that all measurements are made at the same temperature, and thus there is no need to "adjust" each individual result to some standard temperature. There is a corresponding disadvantage, since all measurements are made at 26.9°C while the standard temperature for such data is 25.0°C.

Several practical advantages also obtained from the choice of an isothermal, phase change type of calorimeter. The mechanical construction of the calorimeter can be rigid, and, as in the calorimeter under discussion, the construction can be all welded. Later experience proved that the welded construction is not necessary as Teflon gasketed joints may be used, but the all welded construction is a definite convenience.

In the conventional solution calorimeter one solution is contained in a pipette submerged in the other solution. These pipettes have taken several forms, but the most common seems to be a glass cylinder sealed on each end with a thin film, sometimes of gold or platinum, or more recently of Mylar. To initiate the reaction these films are ruptured by one means or another. This permits mixing of the two solutions. A serious limitation to this method of containing the two solutions is that the entire assembly must be removed, cleaned, dried, and reassembled between each measurement, or every few runs in the cases

where multiple pipettes are used.

In the calorimeter described in this thesis this limitation was overcome by redesigning the pipette. The design adopted was a cylinder closed at each end by stoppers, but with a tube for filling or emptying the pipette. To make one run of a series this procedure was followed. The stoppers were closed and the contents of the pipette removed by suction. This sample was put aside for analysis. The pipette was refilled with the appropriate solution, making sure that it was full by overflowing some of the solution. A small portion of the sample withdrawn was added to the reaction vessel in order to make it overflow, ensuring that the reaction vessel was also full. At this point in the experiment the stirrer was turned on, and allowed to run at least thirty minutes to establish a steady state in the calorimeter. Fore period drift was then measured, the pipette opened, and the aft period drift measured, completing the particular run. Using this calorimeter one run in a series could be completed in sixty to one hundred and twenty minutes, depending on the time that was required to reestablish steady state after the reaction was completed. This timing is to be contrasted with the three days which is usually required for making one or two runs with the conventional calorimeter.

By using fixed volumes of solution in the pipette and in the reaction vessel another saving in time was achieved. The density of each solution involved was measured (normally during the time that the calorimeter was coming to steady state). From the knowledge of the concentration of the solutions used during a run, the densities of these solutions, and the volumes involved it is possible to calculate

the concentration of the resulting solution. After a series of five runs there was no statistical difference (at 95% confidence level) between the analyzed concentration of the final solution and that calculated on the basis of material balances as described above. Thus it is not necessary to analyze every solution.

As mentioned above, diphenyl ether is not a good energy transfer medium. Therefore, the outer wall of the reaction vessel, which forms the inner wall of the diphenyl ether chamber, was machined to have a large number of fins. This was a difficult machining job, but it was felt to be necessary. The results seem to justify this assumption. In calibration experiments, sulfuric acid was reacted with an excess of sodium hydroxide. Under the conditions used this resulted in the release of something in the order of 2400 cal. Some of these runs were followed for two hours after opening the pipette, i.e., mixing the acid and base, but steady state was achieved in all cases in the order of forty five minutes after start of the reaction. This indicates that the energy liberated by the reaction had been completely transferred to the diphenyl ether in this time. In the reactions of interest, that is the dilution experiments, smaller quantities of energy were involved, with more rapid reestablishment of steady state.

Two features of the plumbing deserve mention. After assembly of the calorimeter it was found that the diphenyl ether mantle froze in such a way that the tube leading into the bottom of the diphenyl ether chamber became blocked. The block probably was at the lower end of the finned portion, as the clearance between the fins and the surrounding cylinder was of the order of 1/16 in. In any event it was necessary to

install a "bypass" so that liquid diphenyl ether could enter the chamber from the top as well as from the bottom. A valve was installed in this bypass so that it could be closed off during normal operation of the calorimeter, but in practice it was left open.

Also in the plumbing was a glass bulb of about 200 cm^3 capacity. This was installed for two purposes. In the first place it acted as a "buffer" so that air saturated diphenyl ether from the balance pan would not be drawn into the calorimeter proper. The other function which this bulb served was to prevent air from entering the diphenyl ether chamber in the event of catostrophic failure of the thermostat - as for instance during a power failure.

The outlet of the plumbing system to the balance consists of an 1/4 in. aluminum tube dipping into a beaker of diphenyl ether on the balance pan. The final five inches of the tube were turned down to an outside diameter of 0.150 in. in order to minimize displacement effects. Also the turned finish of the aluminum tube was more true than original tube, making the displacement correction a much smoother function. In fact it turned out to be almost linear.

As the above descriptions indicate, it proved possible to meet most of the design objectives for the isothermal, phase change calorimeter. Over all the calorimeter proved to be capable of rapid operation.

CHAPTER IV

DATA HANDLING SUBSYSTEM

In order to comply with the design philosophy of the calorimetric system it was necessary to develop a method of reducing the data which would be rapid, which would not impair the precision of the measurements, and which would not be subjective. These requirements dictated the use of a high speed digital computer. As the Burroughs B 5500 at the Rich Electronic Computer Center was available to students, it was decided to write programs to be run on this machine. The programs were written in "Extended ALGOL 60 for the Burroughs B 5500."

The data reduction falls into three steps, and so three major programs were written. The break between steps was primarily dictated by the necessity of intervention by the user. The programs were so written that each produced cards as output. After editing, these cards were used as input for the next program.

The original observations were recorded on special forms. The data from each calorimeter run was punched on cards from these forms. From this point on in the data reduction procedure all intermediate recording of results was on cards. Naturally the programs produced printed output as well as cards, but this output was only for the convenience of the experimenter.

The first program is the "Calorimeter Data Reducer." A detailed discussion of this program will be found in Appendix A but a brief

description of what the program does will be given here.

The inputs to the program are the time-weight points recorded during the calorimter run. Each set of data from a run also includes the concentration and density of the two initial solutions, and the density of the final solution. In the case where a series of runs was made such that the final solution from one was one of the initial solutions of the next run, the concentration and density are recorded as all 9's. The program interprets this to mean that the data found for the previous run should be used in this run. This feature makes it unnecessary to determine the concentration of intermediate solutions by chemical analysis.

The ouput of the Calorimeter Data Reducer is a set of cards, one for each calorimeter run, which gives the run number, the ΔQ for this run, the uncertainty in ΔQ for this run, and data on the concentrations of all three solutions involved in this run. Also given is the number of moles of salt in each solution. The printed output gives a table for each run. In the heading of the table are given the data on each solution, number of moles of salt, the weight, the molality and the density. The ΔQ and standard deviation follow, along with the equations for the fore and aft period drift rates. The heading concludes with the reference values for this run, the start time, weight reference, and time of opening the pipette. The body of the table lists the clock and relative time, observed, corrected and relative weight, and the weight/time differential for each point. After the tables for each run there is a summary table, which gives the same data as are given on the output cards.

Cards from the Calorimeter Data Reducer program are used as input

for the Relative Molal Enthalpy Calculator, after suitable editing. The editing must be done by the experimenter. The object of the editing is to arrange the cards, and therefore the solutions, in such an order that the relative molal enthapy of two of the solutions involved in each run are known or can be calculated by a close interpolation. The starting points are the abritrary temporary standard, and pure water. Therefore the first run considered must involve these.

The Relative Molal Enthalpy Calculator program is described in detail in Appendix B. The program calculates the enthalpy for each new solution which is encountered in going through the data cards. The enthalpy, the uncertainty in the enthalpy, the concentration and the square root of the concentration are entered in a table internal to the program. A serial number is also entered for each solution. After the program has considered all of the data cards the table is listed, and cards are punched containing the table one line to a card. These cards may be used to input a starting table to Relative Molal Enthalpy Calculator program or they may be used for other purposes, for example as input data the Curve Fitting program. The Relative Molal Enthalpy Calculator program is general in that it can be used to process the data from any calorimetric experiments which involve the mixing of two solutions to form a third.

Nonlinear least squares techniques are employed in the Curve Fitting program. This program is general, in that any function can be inserted into the program. The only restrictions are that the function giving the dependent variable in terms of the independent variable and the adjustable parameters must be expressed in ALGOL, and that the

partial derivative of this expression with respect to each of the adjustable parameters must also be expressed in ALGOL. A more detailed explanation of this program is given in Appendix C. The Curve Fitting program is used for determining the equation used in extrapolating the molal enthalpy to zero concentration, in order to determine the necessary shift in the zero of the enthalpy scale.

Inputs to the Curve Fitting program are the X - Y points to be fitted, the Levenburg weighting factors (which will be discussed in Appendix C), and two logical values to specify whether the fit will be relative or not, and whether it will be weighted or not. If the weighted option is chosen the uncertainties in the Y values must be inputed with the X - Y points. Estimates of the values of the parameters must also be given. The output of this program is all printed. The values of the parameters after adjustment are given, with the standard error of the fit, followed by the X values, the Y values, the calculated values of Y using the adjusted parameters, and the difference between the observed and calculated Y values. The program will also indicate how many times the Levenburg weighting scheme was applied. For a description of this scheme see Appendix C.

In summary, the data handling subsystem consists of three major programs. The first program is highly specific, in that it uses constants related to the volumes of the calorimeter, to the set of weights used with the balance, and to the salt under investigation.

The second program is not as specific, in that it can process data from all calorimetric experiments involving the dilution of one solution with another to give a third.

The third program is completely general as it can be used for any curve fitting application. Specific equations are included in it to provide specific curves.

In addition to the three major programs, several minor programs were written. These included a program to generate a table of vapor pressure of diphenyl ether as a function of temperature, a program to derive the polynomial used to correct weights for the displacement effect, and various table generator programs.

CHAPTER V

RESULTS ON POTASSIUM NITRITE

Potassium nitrite, KNO_2, was chosen as the salt used in tests of the calorimeter for several reasons. It is of interest because of some of its chemical properties. For one thing, a saturated solution of KNO_2 is something over 36 molal, more concentrated than most salts. Another point of interest is that KNO_2 has not been available in high purity until recently. This factor is explored more fully in Appendix E, which describes the preparation of KNO_2.

Not a small consideration was the fact that Dr. Ray was interested in KNO_2 in connection with some of his research. Since Dr. Ray was advisor for this research at the time, his interest carried weight.

Potassium chloride has been proposed as a standard substance for solution calorimetry. KNO_2 is similar to KCl in some of its properties, and this similarity also influenced the choice.

A plot of the data is presented as Figure 7, where the Apparent Molal Enthalpy relative to the temporary standard is plotted as a function of the square root of the molality of each solution.

Table 1 presents selected values of the Apparent Relative Molal Enthalpy of KNO_2 solutions. The reference state used is the arbitrary temporary standard (17.42 molal). Note that the standard state for electrolyte solutions is the infinitely dilute solution, and this is not included in the given table.

Table 1. Selected Values of Relative Molal Enthalpy of Potassium Nitrite Referred to the Temporary Standard (17.4 M)

Concentration (moles/kg. H_2O)	Square Root Concentration	Relative Molal Enthalpy (cal/mole)	Uncertainty
0.080	0.282	-13	227
0.154	0.393	680	78
0.223	0.473	910	71
0.289	0.537	1012	48
0.348	0.590	1094	50
0.774	0.880	1230	13
1.000	1.000	1145	677
1.108	1.053	1172	21
1.115	1.056	1171	9
1.138	1.067	1167	9
1.529	1.237	1100	9
1.866	1.366	1025	10
2.269	1.506	973	7
2.602	1.613	916	6
2.993	1.730	853	6
3.320	1.822	766	7
3.699	1.923	751	6
4.021	2.005	711	5
4.386	2.094	670	5
5.053	2.248	603	5
5.699	2.387	543	5
6.323	2.515	490	4
6.926	2.632	443	4
8.324	2.885	343	6
9.438	3.072	332	16
10.54	3.247	315	20
11.64	3.411	299	21
12.29	3.506	285	23
12.72	3.566	279	22
13.78	3.712	260	23
17.42	4.174	0	Std.
36.18	6.015	- 20	98

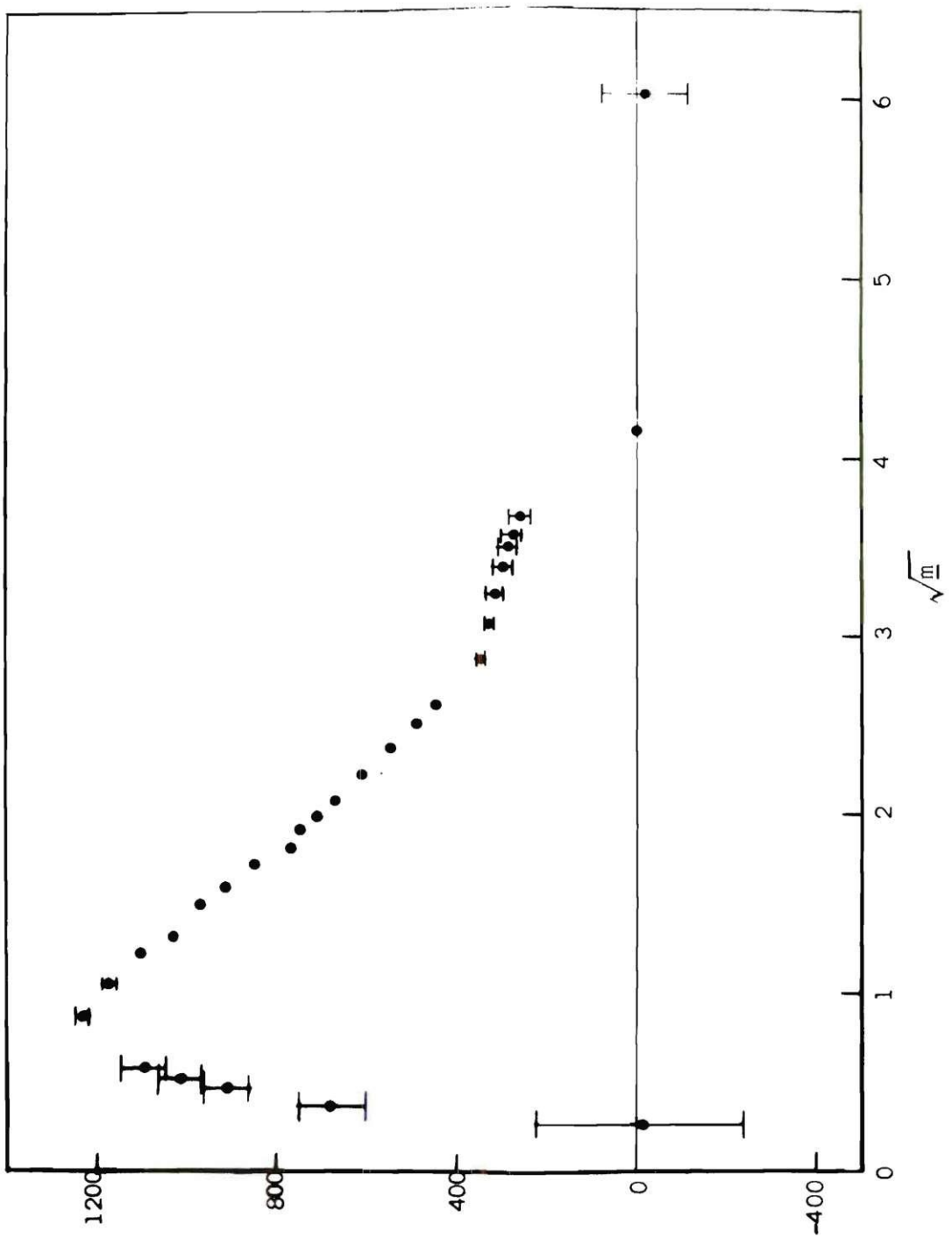

Figure 7. Relative Apparent Molal Enthalpy of KNO_2 vs. Square Root of Molality.

In order to "correct" the observed enthalpies to the infinitely dilute standard state an extrapolation procedure must be used. The data at the lowest concentrations measured are extrapolated, by one technique or another, to infinite dilution, or zero concentration. This gives the numerical value of the enthalpy of the arbitrary temporary standard referred to zero concentration. All of the other enthalpies are then "corrected" or adjusted by this amount.

Unfortunately the data collected in this research were not good enough to be used in such an extrapolation. Only one point under 0.1 M and only five points of less than 0.5 M were obtained. Since the enthalpies are on a molal basis, the uncertainties in the low concentration region of the data are very large. Even recourse to a theoretical slope of the extrapolation line did not give reasonable results. Therefore, the present data can not be corrected to the infinitely dilute standard state.

There are several theoretical treatments which may be used to guide the extrapolation. Even though they were not used in this work a discussion of three of the theories is presented as a guide to using the Curve Fitting program which is a part of the program package of the calorimeter system.

One could use a "simple minded approach" and fit the observed data to a polynomial of second or higher degree. This could be done on a molal basis, that is using enthalpy-molal concentration data, or it could be done in powers of the square root of concentration. The latter method at least partially acknowledges the theoretical development of Debye and Hückel.[2]

Lewis and Randall[3] present an equation which is essentially a polynomial

in the square root of concentration. A theoretical coefficient for the first degree term is used, but the coefficient of the second degree term is derived from the data. Of course the intercept, the zero degree term, is also adjusted to agree with the data. The theoretical coefficient given by Lewis and Randall is derived from the ΔG_{el} of the Debye-Hückel theory by application of the Gibbs-Helmholtz equation. They consider the dielectric constant of water and the density of the solvent as the only temperature dependent factors in the expression for ΔG_{el}. Of course, temperature appears as an explicit function. As all of the physical constants included in the expression are known, an exact value for the coefficient can be calculated.

The expression given by Lewis and Randall[3] is

$$H - H^{\circ} = A_H \, m^{3/2} \, (1 + m^{1/2})^{-1} - \frac{\sigma(m^{1/2})}{3}$$

$$- 2.303 \, RT^2 \, \frac{dB}{dT} \, m^2$$

where $A_H = - 2.303 \, RT^2 \, A_\gamma \, 3 \left(\frac{1}{T} + \frac{\partial \, \ell n \, D}{\partial T} + \frac{\alpha}{3} \right)$

A_γ = the "Debye-Hückel" coefficient

D = the dielectric constant of water

$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)$

$\sigma(y) = \frac{3}{y^3} \left(1 + y - \frac{1}{1 + y} - 2 \, \ell n(1 + y) \right)$

B = a function of the salt

Using the dielectric constant of water calculated from the equation of Wyman and Ingalls,[9] at 27°C, (77.82), their temperature coefficient

for the dielectric constant of water (-4573×10^{-6}), and Handbook[10] values for the other constants, a value of 724.98 cal/$M^{1/2}$ for A_H was found. Vidulich et al.[11] have presented a new value of the dielectric constant of water. This of course leads to a different value for A_H.

Owen and Brinkley[12] performed the differentiation required by the Gibbs-Helmholtz equation using the assumption that the distance of nearest approach, a, is a function of temperature, as well as the other factors considered above. Note that Swanson[7] points out an error in Owen and Brinkley's differentiation. As a value for $\partial \ln a/\partial T$ is not available, Swanson used this as an adjustable parameter in fitting an equation to his observed data. Thus, Swanson essentially used a quadratic equation in the square root of concentration to fit his data.

Swanson[7] presents the following expression for the molal enthalpy of a dilute solution

$$\varphi_H - \varphi_H^o = \left[\frac{NT\,\varepsilon^2}{3D} \sum_i J_i Z_i^2\right]\left[\frac{\tau-\sigma}{2}\left(\frac{\partial \ln D}{\partial T} + \frac{1}{T} + \alpha - \frac{2\partial \ln a}{\partial T}\right) - \frac{3}{2}\tau\left(\frac{\partial \ln D}{\partial T} + \frac{1}{T} + \frac{1\alpha}{3}\right)\right]$$

where N = Avogadros' number

ε = electronic charge (e.s.u.)

J_i = number of ions of species i per mole of solute

Z_i = valence of ionic species i

a = ion size parameter

$$\tau = \frac{3}{(Ka)^3}\left(1/2\ K^2a^2 - Ka + \ln(1 + Ka)\right)$$

$$\sigma = \frac{3}{(KA)^3}\left(1 + Ka - \frac{1}{1 + Ka} - 2\ln(1 + Ka)\right)$$

$$K = \left(\frac{4N^2}{1000\ DkT} \right)^{1/2} \left(\sum J_i Z_i^2 \right)^{1/2} m^{1/2}$$

Either of the above equations may be used to fit an equation to the experimental data using the curve fitting program described in Appendix C. However, since none of them were actually used in the current work no comparison can be made between the various approaches.

CHAPTER VI

EVALUATION AND RECOMMENDATIONS

Evaluation of the Calorimeter System

Evaluation of the calorimeter system in terms of the project goals is a somewhat disappointing task. To restate the goals they were 1. to build a calorimeter which is fast and convenient to use, 2. to write and check out computer programs to reduce the data, 3. to demonstrate the adequacy of the system on KNO_2, and 4. to leave an operating "system."

The system which was built is indeed fast and reasonably convenient to use. However, it was not possible to prove that the system would be fast under good environmental conditions. Thus, it might be found that the system would require excessive time to come to steady state before opening the pipette, or that the time needed for the calorimeter to return to a steady drift rate after the reaction is longer than that used in the experiments.

Evaluation of the second goal of the project, that is to write and check out the computer programs, is more satisfying. The programs were written, and worked on all test examples run as well as on the data collected from the calorimeter.

The results of the experiments using the new calorimeter were not of the precision expected of a "good" solution calorimeter. The fact that these results were obtained in a short period of time justifies the claim that the calorimeter design is good, and the

discussion of errors given below supports that claim that under better laboratory conditions the calorimeter would be satisfactory. Thus, it may be said that the demonstration goal was partially met.

The environment of the calorimeter was not under good control, and the variations noted could not be definitely ascribed to the calorimeter or to the variations of the environment. The temperature of the room varied, and this would naturally effect the drift rate of the calorimeter, as room temperature variations were not averaged out by the thermostat. Also, due to vibration of the floor and the resulting difficulty in achieving the precision which the balance should provide, it is impossible to say whether the observed variations in drift rate were real, due to temperature changes within the thermostat, or whether they were random "noise."

A major difficulty in operating the calorimeter was the time required to "tune" the system -- to adjust the thermostat, to get a good mantle of diphenyl ether, and in general to get the system ready to make a series of measurements. There was a complex interaction between the setting of the thermostat, the setting of the thermostat on the room air conditioner, and the average and extreme temperatures of the atomosphere outside the laboratory. The interaction could only be dealt with on an intuitive basis, and it was time-consuming to develop the necessary expertise.

However, when all of the factors influencing the calorimeter were under control it was possible to make the series of measurements to define the heat of dilution of potassium nitrite in four weeks of operation. This included the time needed to set up solutions, to run

the calorimeter, to punch the data cards and to run the data reduction program.

As indicated above, the calorimeter was not as precise as desired. A rather horrible example of the lack of precision is provided by a series of opening experiments. In these experiments the same solution was in both the reaction vessel and the pipette. The energy change caused by opening the pipette without any "reaction" was measured. A series of nine experiments were performed, five on solutions and four on water. The average energy change expressed in grams of diphenyl ether (1 g is equivalent to 239.85 cal), of the nine experiments was 0.0175 g with a standard deviation of 0.0456 g. The extreme measurements were -0.0210 g and +0.1233 g, both measured on solutions. In the water experiments there were two positive and two negative results.

In three experiments where H_2SO_4 was reacted with an excess of NaOH the average change was 9.04986 g with a standard deviation of 0.02353 g. This not only represented three independent experiments, but two different diphenyl ether mantles.

Thus, the absolute value of the standard deviation of a series of experiments seems to be about constant at 0.02 to 0.04 g (5 to 10 calories). Under ideal conditions the sensitivity of the balance used is about 0.0002 g (0.2 mg). The difference of two orders of magnitude between the expected sensitivity and the observed standard deviation is attributed to the lack of a stable platform for the balance. In turn the lack of stability is blamed on the laboratory floor, which shook under the influence of vacuum pumps, people walking

in other parts of the building, and other undetermined disturbances. If a stable platform for the balance had been used standard deviations of 0.05 to 0.1 calories would be expected.

The reported uncertainities in the ΔQ's are not even as good as the above discussion indicates because they include the uncertainty in the energy change associated with opening the pipette. The large scatter in the measured values of this energy change is ascribed to poor temperature control of the thermostat. The slope of the fore period equation for two of the opening experiments were 0.0133 and 0.0180 g/min even though the experiments were run about thirty minutes apart. These slopes represent energy input to the calorimeter from the stirrer and from "heat leaks." The energy input from the stirrer was constant since the stirrer was driven at a constant speed by a synchronous motor. Thus, the difference in energy input must be ascribed to the changes in the "heat leaks," and these changes in turn must be due to changes in the temperature of the thermostat.

If better temperature regulation were achieved, the uncertainty in the energy change due to the opening of the pipette could be reduced. An order of magnitude reduction would result in an uncertainty of about 1 calorie in the "opening energy" and thus in all of the measured ΔQ's. Greater reductions in the uncertainty of the "opening energy" would not result in corresponding reductions in the uncertainty of the ΔQ's as the sensitivity of the balance would become important.

Finally the goal of leaving an operating system had to be abandoned for at least two reasons. First the system could not really be said to be operating as it was. Secondly, undesirable as the

laboratory was for calorimetric measurements, other research groups needed the space, and the calorimeter had to be "pushed into the corner." It would involve a major effort to put the calorimeter in operating condition again.

Recommendations for Future Work

During the evaluation of the calorimeter system as well as during the use of the sytem a number of suggestions for future work were examined. Some of these suggestions are given for the benefit of anyone interested in this system, or modifications of it. These suggestions fall into several groups on the basis of what system is to be considered. In the first group would be the recommendations to anyone trying to use the calorimeter used during this investigation. Obviously two recommendations would take highest priority, i.e. to get a more stable location and to provide better temperature control.

Stability of the laboratory floor is important because the useful sensitivity of the balance is dependent on the amount of vibration to which the balance is subjected. It is self-evident that a stable platform for the balance can not be based on an unstable floor.

Less apparent from the report of the work, but very apparent to the experimenter is the adverse effect of unstability on the vacuum system. The glass manifold of the vacuum system broke a number of times due to strains induced by the "flexible" floor. Such breaks caused long delays.

Better regulation of the temperature could be achieved in at least two ways, both assuming that the calorimeter would be installed

in an air-conditioned room. Air-conditioning would provide a reasonably constant ambient temperature making the task of the thermostat much less demanding. The first approach to better temperature regulation would be to improve the air thermostat. This could be accomplished by insulating the thermostat box, and by modifications to the temperature controller. Such modifications should include better voltage regulation for the controller and possibly relocation of the thermistor.

Perhaps a better approach would be to employ a water bath as a thermostat. Such a thermostat would require some modification to the "plumbing" of the calorimeter, but this in itself would not be undesirable. Also, a different suspension for the calorimeter would have to be devised.

More extensive modifications might include installation of some sort of "plumbing" to allow for periodic repurification of the diphenyl ether. In the course of extensive use, some air saturated diphenyl ether would be likely to make its way into the diphenyl ether chamber. This would be catastrophic. Formation of air bubbles in the diphenyl ether chamber would destroy the whole basis of the phase change method of measuring the energy change since the air would be compressible, and therefore of changing volume. Periodic redistillation of the diphenyl ether could prevent such a catastrophe.

Another modification would be to weigh mercury rather than diphenyl ether. The greater density of the mercury would increase the sensitivity of the calorimeter. However, the use of mercury would not be without drawbacks. The capacity of the system would be decreased

by the same factor by which the sensitivity would be increased since the capacity of the balance is the limiting factor. Also there is the very real danger of reaction between the mercury and the diphenyl ether or between the mercury and the aluminum of the calorimeter.

Even more exotic modification might include using an automatic balance to record weight changes. This could be combined with some sort of recording device which would prepare the data for direct use by a computer. One further step would be to combine the calorimeter system with a so-called real time computer system, so that the data would be entered directly into the memory of the computer, with answers being provided within seconds after the completion of the experiment.

If a new calorimeter were built, two major recommendations would be made.

First would be to abandon the all metal, welded construction employed in the current calorimeter. Teflon or soft metal can be used as gasket material so that a jointed construction could be used. This would alow construction from glass and metal. Thus it would be possible, and desirable, to construct the outer cylinders from glass pipe. This would allow visual observation of the diphenyl ether mantel, as well as permitting some simplification of the construction.

Secondly, it is recommended that polyethelyne be used to coat the inside of the calorimeter rather that Teflon. Polyethylene is applied at much lower temperatures than Teflon, and is considerably easier to control during the coating process. As something over two years was devoted to applying the Teflon coating to the calorimeter, this recommendation is made with feeling.

In conclusion, the author can only wish luck to any experimenter who undertakes reactivating his calorimeter, or building a new one.

APPENDIX A

CALORIMETER DATA REDUCTION PROGRAM

This program takes the raw weight - time points as input, and generates the ΔQ for each calorimeter run as output. It also converts concentration and density data from the starting solutions to concentrations for the intermediate solutions.

As part of the calculations the raw weights are first corrected for actual weights in the set used, and then the corrected weight is adjusted for the displacement effect of the delivery tube in the beaker of diphenyl ether. The observed time - clock time - is also converted to a relative time expressed as minutes and decimal fractions of minutes.

In the following writeup reference will be made to cards by number. These numbers may be found on a listing of the program. Interested readers are referred to the program for such a listing. Note that the card numbers increase in increments of one hundred, to allow for insertion of additional cards if desired. Reference will be made as though the increment were one. That is, the card which is numbered as "DR 2700" will be referred to as card 27. Note also that the program is written in "Extended Algol 60 for the Burroughs B 5500."

The necessary declarations are on cards 1 through 49. The input file is labeled "CARDS" (card 2). There are two output files "PRINTER" (card 3) which is declared as a printer backup tape, and "PUNCH" (card 4) which is declared as a card punch.

Format "FORM1" (card 13) is for the input cards. This card should

be changed if a different format is desired.

Procedure "DATER" (cards 50 - 79) places the date of the computer run, the processor and input-output (I/O) times at the end of the output.

Procedure "CWT" (cards 80 - 119) takes the observed weights and corrects them for the inaccurate weights used. The particular corrections are those for Set 21-B from the Analytical Chemistry group. Cards 89 through 99 make the adjustments for the 1 through 100 gram weights. Card 99 selects a branch to one of the labeled statements (cards 100 - 117) depending on the rider setting in the observed weight. Card 117 adjusts the chain reading. Cards 118 and 119 are the necessary housekeeping details for the procedure.

Procedure "LSTSQ" (cards 120 - 149) is called from several places in the program to determine the "best line," in the least squares sense, through a set of weight - time points. These points may be those which define the fore period drift rate, or some other line. The line is defined by the variables "M" and "B" in the form:

$$CY_i = X_i \cdot M + B \qquad \text{(A-1)}$$

The procedure also determines the standard error of the points and the derived line. The standard error is defined below.

$$\text{Std. Er.} = \sqrt{\sum_i \frac{(CY_i - Y_i)^2}{N - 2}} \qquad \text{(A-2)}$$

where CY_i = the value calculated from Equation (A-2) using X_i as an argument

Y_i = the observed value of Y corresponding to X_i

N = the number of $X - Y$ points .

The values of "M", "B", and "SCATTER" - the standard error - are returned by the procedure to the calling point.

Cards 150 through 157 set up some housekeeping details. The array "A" contains the coefficients of a sixth degree polynomial used to calculate the correction to the adjusted weight made necessary by the displacement effect. "SIG" is the value used to reject points which fall outside of a certain probability. The value 1.65 is chosen so that approximately 10% of "true" points would be rejected. "MOLWT" contains the molecular weight of the salt under investigation, and thus this card would have to be changed if any other salt were run.

"LIMIT" limits the number of points in a sequence which can be rejected. It is assumed that if more than this number of points in a sequence are "bad" then the curve is no longer a straight line, that is that some of the reaction energy is included in the change of energy along with the drift. "BASEWGH" is set to the corrected reading of the balance when the beaker contains the minimum amount of diphenyl ether. This weight represents the lower limit of balance readings, and is used to define relative weights.

The data for all of the calorimeter runs to be calculated during a given computer run are read in by cards 158 through 172. Card 161 reads in the run number, the date of the run, the concentrations of the two starting solutions, and the density of the two starting solutions and the final solution. Note that if this run is not the first of a series the concentration and density of one of the starting solutions may be arbitrarily set very large to indicate that the values calculated for the final solution of the previous run should be used for this solution.

The loop defined by cards 162 through 171 reads the set of weight-time points for each run. The end of each set is indicated by a card which has "END" punched in columns 78 - 80. The data card which follows gives the solution information for the next run. The last set of data cards is followed by the system "END card" rather than the END card described above. This transfers control of the program to card 172 which closed and releases the card reader.

Cards 174 through 192 calculate the molality of the final solution, the number of moles in each solution, and the weight of each solution from the molality and density data read in and from the volumes of the two compartments of the calorimeter. The volume of the pipette, 84.03 cm^3, is used by card 184, while the volume of the reaction vessel, 1071.6 cm^3, is used by card 186. Naturally these cards would have to be changed if the calorimeter is modified. Card 192 prints out the values read and calculated.

Clock time in the form of hours, minutes, and seconds is transformed to relative time in minutes and decimal fractions of minutes by cards 194 through 218. The relative times are referred to the nearest whole minute previous to the first recorded time. Note that the first time in the data set is the time of opening of the pipette, and that the time-weight pairs start with the third card in the data set. The relative times are "adjusted" to allow for the fact that there are only sixty minutes in an hour although the time is expressed in a three or four digit integer of hours and minutes, that is in the so-called military time.

Starting at card 220 and going through card 228 is the section

which converts the observed weight to corrected and adjusted weights by means of procedure "CWT" and the sixth degree polynomial. The corrected and adjusted weights are stored in the array "W". The corresponding relative times are stored in the array "T".

Procedure "LSTSQ" is called by card 230 to establish the first estimate to the fore period line. The last six points before "TZERO," the time of opening the pipette, are used to establish the line. Cards 233 through 246 test each of the points before the opening time against the calculated line generated by "LSTSQ". If the weight, which is taken as the dependent variable, differs from the line by more than "SIG" times the standard error, "S", then that point is rejected. The points which are not rejected are put into the arrays "TT" and "WT", which are then passed to procedure "LSTSQ" by card 247. Procedure "LSTSQ" returns the slope and intercept of the fore period line in "MF" and "BF" respectively, and the standard error in "SF".

Cards 251 through 281 calculate the equation for the aft period drift in a manner completely analogous to that described above for the fore period except that two estimates to the aft period line are made rather than the one made for the fore period. This is to allow for the fact that the energy change due to the reaction in the calorimeter shows up as a rapid change at the beginning, but only approaches the drift rate asymptotically. Thus, the two approximations to the line help to reject points which are not on the drift rate line, but are on the change over from reaction to drift.

"FUDGE" is set by card 282 to the calibration factor of the calorimeter. The value used here is 239.85 calories per gram of diphenyl ether.

This value is the average of the values calculated from the reported calibration factors of Jessup[13] and of Giguere et al.[14] The observed energy change, "HEAT" and the standard error associated with it, "SD", are calculated by cards 285 through 287. Note that the factor 0.002079 which is included in the standard error is the uncertainty in the energy of opening the pipette, while the factor 0.0175051 is the average value of this energy change.

Output is generated by cards 289 through 300. This takes the form of the data on each calorimeter run followed by the data on the solutions involved, followed by the observed energy change and associated uncertainty followed by the reference points, that is the base time, base weight and the opening time, finally followed by a listing of the time-weight points with the quantities derived from them - the relative time, corrected and relative weights, and the differential change in weight with time. After the full data for each run is outputed a summary of the data from all calorimeter runs included in this computer run is printed, with some of the data being punched in cards at the same time. (Cards 293 - 299.)

Finally "DATER" is called to put the timing information on the printed output.

Figure 8 shows the output for a typical calorimeter run.

RUN NUMBER 21 DATE 11/19/66

SOLUTION 1 0.8672 MOLES KNO2 IN 123.59 GRAMS OF SOLUTION,
OR 17.41820 MOLAL: DENSITY = 1.4708
SOLUTION 2 3.4928 MOLES KNO2 IN 1241.45 GRAMS OF SOLUTION,
OR 3.69927 MOLAL: DENSITY = 1.1585
SOLUTION 3 4.3600 MOLES KNO2 IN 1365.04 GRAMS OF SOLUTION,
OR 4.38643 MOLAL: DENSITY = 1.1837

DELTA Q = -294.14 STANDARD DEVIATION = 10.94

FORE PERIOD EQUATION: WEIGHT = 0.0083 x TIME + 53.78 STD. ERROR = 0.00070
AFT PERIOD EQUATION: WEIGHT = 0.0099 x TIME + 52.56 STD. ERROR = 0.00006

START TIME = 1651
WEIGHT REFERENCE = 117.9579
TZERO = 7.50

CLOCK TIME	RELATIVE TIME	OBSERVED WEIGHT	CORRECTED WEIGHT	RELATIVE WEIGHT	DIF.
1651: 7	0.12	171.9100	171.9120	53.7879	0.000@+00
1651:55	0.92	171.9150	171.9169	53.7928	6.155@-03
1652:36	1.60	171.9200	171.9219	53.7977	7.206@-03
1653:12	2.20	171.9250	171.9268	53.8027	8.207@-03
1654: 8	3.13	171.9350	171.9367	53.8125	1.055@-02
1654:38	3.63	171.9400	171.9416	53.8174	9.848@-03
1655: 5	4.08	171.9450	171.9465	53.8224	1.094@-02
1655:39	4.65	171.9500	171.9515	53.8273	8.690@-03
1656:26	5.43	171.9550	171.9564	53.8322	6.286@-03
1656:55	5.92	171.9600	171.9614	53.8371	1.019@-02
1657:32	6.53	171.9650	171.9663	53.8421	7.985@-03
1658: 7	7.12	171.9700	171.9712	53.8470	8.441@-03
1659:48	8.80	171.5000	171.5019	53.3790	-2.780@-01
1704:16	13.27	171.0000	171.0021	52.8807	-1.116@-01
1709:22	18.37	170.9400	170.9414	52.8202	-1.186@-02
1710:45	19.75	170.9350	170.9365	52.8153	-3.560@-03
1714:15	23.25	170.9343	170.9358	52.8146	-1.970@-04
1714:45	23.75	170.9343	170.9358	52.8146	0.000@+00
1715:50	24.83	170.9400	170.9414	52.8202	5.182@-03
1717:25	26.42	170.9500	170.9513	52.8300	6.220@-03
1717:57	26.95	170.9550	170.9562	52.8350	9.233@-03
1718:32	27.53	170.9600	170.9612	52.8399	8.441@-03
1719: 2	28.03	170.9650	170.9661	52.8448	9.848@-03
1719:34	28.57	170.9750	170.9710	52.8497	9.233@-03
1720: 4	29.07	170.9750	170.9760	52.8547	9.848@-03
1720:34	29.57	170.9800	170.9809	52.8596	9.848@-03
1721: 2	30.03	170.9850	170.9859	52.8645	1.055@-02
1721:34	30.57	170.9900	170.9908	52.8694	9.233@-03
1722: 3	31.05	170.9950	170.9957	52.8744	1.019@-02

Figure 8. Output of Calorimeter Data Reduction Program for Run 21.

APPENDIX B

RELATIVE ENTHALPY CALCULATION PROGRAM

The input to the Relative Enthalpy Calculation Program is the set of cards containing the data from each calorimeter run. These cards are produced by the Calorimeter Data Reducer Program.

It is necessary for the experimenter to arrange the cards as the program considers one card at a time. The first card should be one that refers to the dilution of the temporary standard solution with water. Following this card can be a series representing a series of calorimeter runs. In this manner a table of enthalpy values is constructed. After the original series is defined subsequent cards representing other solutions may be read.

The output of the program is a deck of cards containing the table generated. This table is also printed out with appropriate headings. Figure 9 shows this table for the experiments on KNO_2.

If desired, a partial table may be read into memory from cards, and then additional values calculated. The format of the output cards is the same as that of the input table.

Description of the program is given below, following the same conventions used in Appendix A.

Cards 1 through 23 are the necessary declarations. The input file is "FFHCARD", though it is referred to as "CARD" within the program. The output files are "FFHPRNT", a printer backup tape, and "PUNCH", the card

CONCENTRATION	SQUARE ROOT CONCENTRATION	PHI L	"STANDARD ERROR"	SERIAL NUMBER
0.0000	0.0000	0.00000	0.00000	2
0.0797	0.2823	-100.83843	386.81009	28
0.0798	0.2825	27.00375	176.56658	22
0.1541	0.3926	629.99214	175.44185	27
0.1542	0.3927	696.17338	58.29408	21
0.2233	0.4725	887.43117	104.04593	26
0.2234	0.4727	922.29523	56.80623	23
0.2878	0.5365	1012.04624	67.23027	24
0.2880	0.5367	1012.27948	67.23040	20
0.3479	0.5898	1091.19949	58.60407	25
0.3482	0.5901	1095.81497	43.67889	14
0.7741	0.8798	1230.44520	12.61650	3
1.1080	1.0526	1171.56399	16.01159	29
1.1153	1.0561	1171.26430	9.54022	13
1.1383	1.0669	1167.15628	9.54222	19
1.5294	1.2367	1099.84708	8.92876	4
1.8662	1.3661	1024.75983	11.84244	16
2.2131	1.4876	859.18362	51.34417	31
2.2693	1.5064	972.89064	7.29668	5
2.6020	1.6131	916.44300	7.03481	15
2.9931	1.7301	852.72752	6.32876	6
3.3203	1.8222	766.01299	7.88549	18
3.6993	1.9234	751.69849	5.67163	7
4.0207	2.0052	711.45661	5.56200	17
4.3864	2.0944	669.64913	5.19008	8
5.0529	2.2479	603.05453	4.81884	9
5.6989	2.3872	542.60163	4.52388	10
6.3234	2.5146	490.08611	4.28091	11
6.9256	2.6317	442.74825	4.07871	12

Figure 9. Output of Relative Enthalpy Calculation Program for KNO_2.

CONCENTRATION	SQUARE ROOT CONCENTRATION	PHI L	"STANDARD ERROR"	SERIAL NUMBER
8.0502	2.8372	488.79374	23.29186	42
8.3240	2.8851	343.26774	7.75513	32
8.9047	2.9841	442.54410	23.24003	41
9.4377	3.0721	332.75110	16.46705	33
9.8791	3.1431	381.95121	23.19516	40
10.5439	3.2471	315.16584	19.88063	34
10.9979	3.3163	335.02137	23.15632	39
11.6370	3.4113	298.73825	21.63287	35
12.2897	3.5057	284.98220	23.12283	38
12.7167	3.5660	278.58731	22.58864	36
13.7791	3.7120	260.12247	23.09418	37
17.4182	4.1735	0.00000	0.00000	1
36.1780	6.0148	-19.57334	98.11855	30

DATE RUN APR. 19, 1967
PROCESSOR TIME = 3.17 SECONDS.
I/O TIME = 16.07 SECONDS.

Figure 9. Output of Relative Enthalpy Calculation Program for KNO_2 (continued).

punch. Format "FORM1" is for the input cards. This is the same format as used for the output from the Calorimeter Data Reducer Program. "FORM2" creates the printed heading for the table. "FORM3" is the format for the printed table. "FORM6" is the format for the card output table, and also for the input table if it is used. "FORM4" is used to read in a control card to indicate whether or not a table will be read in as input. See a later description.

Procedure "DATER" (cards 24 - 53) is called at the very end of the program to put date and timing information on the printed output.

Procedure "ADJAR" (Cards 54 - 90) is called to insert a new entry into the table contained in memory. In the program the table is an array "AR". The parameters passed to "ADJAR" are "CON", the concentration of the solution to be inserted, "THATA", the value of the enthalpy of that solution, and "SC", the uncertainty in the enthalpy.

Format "FMT" is referenced if the new concentration to be inserted in the table is the same as one already in the table. This is considered to be an error condition, and causes a message to be printed out, to that effect, and then causes termination of the program, after listing and punching the table as it existed before the attempt to add the erroneous values. Cards 66 through 72 make the necessary test, and perform the transfers. Card 65 determines the position in the table that the new values should occupy, and cards 73 through 80 shift current values in the table to make room for the new values. These values are inserted by cards 81 through 85. The fifth position in the array is used as a serial number to indicate the order in which the entries were made. Cards 86 through 89 increment pointers used elsewhere in the program if necessary.

Procedure "INTP" (Cards 91 - 159) is called when it is necessary to find the enthalpy of a solution by interpolation. The formal parameters of this procedure are "CON", the concentration of the solution whose enthalpy of a solution is known, and "PONT", a pointer which indicates the position in the table where the values for this solution should be inserted. A test is made at card 100 to see if the concentration to be handled is near the ends of the table. If it is, a 3 point Lagrangian interpolation scheme is applied by cards 101 through 130. If not a 5 point Lagrangian interpolation is applied by cards 131 through 155. Card 156 sets "BO" to true to indicate that the solution is now known, and card 158 calls "ADJAR" to insert the newly calculated values in the table.

Card 162 reads a control card to see if a partial table is to be read in or not. If the word "CARD" appears in columns 1 - 4 of the control card a table is to be read in. The cards defining the table would then follow the control card in the input deck. Cards 164 through 168 read in the table. If a table is being read in, a system control card (a DATA FFHCARD card) follows the table. If there is no partial table, the first card in the input deck should have anything but "CARD" in the first four columns. The next card gives the concentration of the temporary standard, and the relative enthalpy of this solution (usually zero). Cards 171 through 181 read in this card and sets up a table containing two entries, zero concentration and the arbitrary standard concentration.

A loop is defined by cards 182 through 285. This loop is executed once for each solution data card. Cards 188 through 199 set pointers for each of the three solutions referenced on a card, as well as setting the

boolean variables "BOOL1", "BOOL2", and "BOOL3" to show whether or not each solution is already in the table.

If either of the two initial solutions are water, i.e., have zero concentration, the section defined by cards 200 through 229 is executed. Tests are made to find which solution has zero concentration, and to find whether the other initial solution is listed in the table or not. If enough data is available the enthalpy of the final solution is calculated by the section cards 260 through 285. Otherwise tests are made to see which interpolation involves the shortest interpolation, and then calls on "INTP" to perform the interpolation.

If none of the solutions have zero concentration the section defined by cards 232 through 259 is executed. Again tests are made to see if enough data exists in the table to calculate the enthalpy of one of the solutions from that of the other two. If not, tests are made to find the shortest interpolation, and "INTP" is called to perform the interpolation.

By the time that control has passed to card 260, the enthalpy of two of the three solutions referenced on one card are included in the table. The section between card 260 and card 285 calculates the enthalpy of the remaining solution using the appropriate transformation of equation (B-1).

$$\Delta Q = n_3 \Phi_{L3} - n_1 \Phi_{L1} - n_2 \Phi_{L2} \qquad (C\text{-}1)$$

The uncertainty in the enthalpy is also calculated using the square root of the sum of the variances of each solution and of the ΔQ, divided by the number of moles.

After all of the data cards have been read control is transferred to card 286. Cards 287 through 291 write out the table with heading on the printer, and punch the table on cards. Card 292 calls "DATER" to provide timing information on the printed output, and card 293 ends the program.

APPENDIX C

NONLINEAR CURVE FITTING PROGRAM

The Nonlinear Curve Fitting Program is a general program. It will fit a function to data when the function and its partial derivatives are given. The program contains several extensions to the standard nonlinear curve fittings algorithms. Margenau and Murphy[15] give an outline of the mathematical development of the conventional nonlinear least squares curve fitting algorithm.

The extensions adapted in the program actually used consist of the Levenberg[16] method to insure convergence and weighting and relative error schemes developed by the author. The Levenberg method consists of modifying the system of normal equations in such a way that the corrections are made smaller, and thus do not "overshoot" and cause divergence of the result. The Levenberg method is applied in two ways in the program. Two "Levenberg weighting factors," "LEV1" and "LEV2" are supplied as input. "LEV1" is applied to the normal equations during every iteration, while "LEV2" is applied only if the sum of the squares of the residuals increases during a given iteration. These weighting factors must be positive numbers greater than or equal to one. If a factor of one is used the effect is that no Levenberg correction is applied. On the other hand if values greater than one are used the solution converges more slowly. Thus it is desirable to use a value of "LEV1" close to one - often 1.01 - and a larger value for "LEV2". The program reduces the Levenberg weighting factors at the end of ten cycles of adjustment if convergence has been steady during those cycles.

Input to the program is in two forms. ALGOL statements defining the function to be fitted, in terms of the independent variable and the adjustable parameters, and of the partial derivatives of this function with respect to the adjustable parameters must be given in the define declaration "FUNT", that is between cards 6 and 14. The other form of input is the set of X - Y points, with variance if weighting is requested, values for "LEV1" and "LEV2", logical values to indicate whether or not weighting and/or relative schemes are to be used, and estimates of the values of the adjustable parameters. The X - Y points are read in under Format "FORM1", one point per card. These are in the file "CARDFH1". File "CARDFH2" contains one card giving the values of "LEV1", "LEV2", "WTD", and "REL". Subsequent cards give the estimates to the values of the adjustable parameters, one to a card.

Output of the program is a series of pages. Each page lists the current values of the adjustable parameters, the standard error, and a table of values of the independent variable (X), the dependent variable (Y), the calculated value of the dependent variable (CY), and the difference between the given and calculated values of the dependent variable. If the values of the Levenberg weighting factors was changed after a number of cycles the new values are printed out, otherwise the number of times that the Levenberg method was applied is listed along with some data concerning each application. These data are useful in judging whether appropriate values of the Levenberg weighting factors had been used.

One page of output is given before the start of adjustment of

the parameters, and then after every ten cycles of adjustment, until final values are obtained.

A card by card description on the program is given below. Cards 1 through 14 concern the function to be fitted. Program declarations follow (Cards 15 - 44). The output file is "PRINT", a printer backup tape, while the input files are "CARDFH1" and "CARDFH2". Format "FORM1" is used to read in the X - Y points, while "FORM2" is used to read in the estimates to the adjustable constants.

Cards 45 through 73 contain procedure "DATER", which prints the date of the run and timing information at the end of the output.

Procedure "SEQ" (cards 74 through 168) solve the set of simultaneous normal equations. The method used is inversion of the matrix of coefficients of the normal equation by elimination, using "best pivitols", and multiplying the vector of the constant by the inverse matrix. If the matrix of the coefficients is singular, control is passed to a label corresponding to "SINGULAR" in the procedure call. This action will terminate the program after putting out an appropriate message.

Procedure "EVAL" (Cards 169 - 186) evaluates the function at each point to obtain a calculated value for the dependent variable, and values for the partial derivatives and residual at each point. If weighted least squares are to be used card 183 sets "D", the residual, accordingly.

The work of the program is done in Procedure "NLLSQ". (Cards 187 - 279). The formal parameters of "NLLSQ" are "X" the independent variable vector, "Y" the dependent variable vector, "WT" the weighting

vector, "C" a vector containing the current values of the adjustable parameters, "S" a matrix which indicates whether or not the Levenberg method was applied in a given cycle, and if so what the final value of the correction factor was, "CY" a vector containing the calculated values of the dependent variable, "D" a vector containing the difference between the given and calculated values of the dependent variable, "N" the number of X - Y points, "M" the number of adjustable constants, "MAX" the number of cycles to be done, "WT1" and "WT2" the values of the Levenberg weighting factors, "LIM" a limit on the relative change in the sun of the squares of the residuals or adjustable parameters, "SSQ" the sun of the square of the residuals, and "WTD", "REL", and "BOO" boolean variables which indicate whether to use weighted or relative schemes, or if the "final" values of the adjustable constants have been obtained. Final values of the constant are assumed to have been obtained when the relative change in the sum of the square of the residuals and the relative change in each adjustable parameters are each less than "LIM". Cards 189 through 201 describe the formal parameters, and declare the necessary local variables. Cards 202 through 205 set up housekeeping details. If the relative scheme is used the section consisting of cards 207 through 224 is executed to construct the matrix of coefficients of the normal equations and the vector of the constants. Otherwise the section from card 225 through card 243 is executed to generate the matrix and vector. The values are stored by cards 244 through 247, and the first Levenberg weighting applied by cards 248 and 249. Card 250 calls "SEQ" to calculate the corrections to the adjustable parameters. Cards 252 and 253 apply the corrections, and card 254 calls "EVAL". If

the sum of the squares of the residuals is greater than that obtained after the previous cycle the section consisting of cards 257 through 270 is executed repeatedly until a lower sum is obtained. This section applies the Levenberg method using "WT2" as a weighting factor. Cards 271 through 278 make various tests and transfers control to the appropriate location.

Cards 280 through 325 constitute a driver for "NLLSQ", and also take care of the input and output. The only section which requires comment is that contained in cards 291 through 295, which calculates the elements of the weighting vector from the variance vector. The weighting factors are scaled so that the smallest variance gives a factor of one, while the larger variances give factors less than one. If a point has zero variance it is given a weight of one.

APPENDIX D

PURIFICATION OF DIPHENYL ETHER

The working medium chosen for the calorimeter was diphenyl ether. Although this material is available in relatively high purity commercially, it was subjected to further purification. This was desirable for several reasons. Diphenyl ether is relatively stable chemically, but there is no history connected with the commercial product. Thus, there is no way of telling how long a time had elapsed between the final step of purification and the time when it was to be used.

As far as use in the calorimeter is concerned, purity is necessary for two major reasons. The first is to insure a sharp melting point over a considerable range of fraction of the charge frozen. Obviously, if the melting point of the diphenyl ether changes during the course of an experiment, not only does the whole calorimeter have to "follow" the change in temperature, but the energy relationships are completely confused.

The other reason for requiring high purity of the diphenyl ether is that the heat of fusion is known for the pure material. If the charge in the calorimeter were impure not only would this heat of fusion not be known precisely, but it would probably be changing as a function of the fraction of the charge melted.

In order to insure purity of the diphenyl ether, several different

methods of purification were employed in sequence. This procedure should insure that no foreign substance was carried all the way through the purification scheme.

The starting material for the purification scheme was Eastman White Label Phenyl Ether. The first step of purification was to stir the diphenyl ether with solid KOH for at least forty-eight hours. This step was designed to remove any residual phenol in the diphenyl ether by forming the potassium salt, which would not distill in the next step.

Approximately 2 liter of diphenyl ether was then loaded into the pot of a packed column still. The still gave about 100 theoretical plates when used with a 3:1 reflux ration. Iron fillings were added to the pot in order to promote good boiling and also to reduce any peroxides which might have formed in the ether. The still was brought up to operating temperature and the diphenyl ether refluxed for at least forty-eight hours to pyrolyze any trace impurities. During this time the ether was allowed to reflux high into the still head by shutting off the cooling water. This ensured that any water absorbed on the walls of the still head was driven out. (The boiling point of diphenyl ether is about 258^{o}C.) After pyrolyzing a cut of about 50 ml was removed. This represented about 2% of the charge, but proved to be more than enough to bring the temperature of the still head up to 258^{o}C, and to maintain that temperature. Product was removed until the pot temperature went up to such a point that it was almost impossible to control flooding. At this point there was about half a liter of material left in the pot. Naturally it was necessary to distill several batches of diphenyl ether since the yield in any one distillation was between one and one and a

half liters.

The distilled ether was introduced into especially constructed tubes for zone refining. The design of the tubes evolved from a number of trials carried out by Mr. Morris Roberts. In the final form the tubes contained three separate compartments, divided by glass bulkheads. In the "pure" end of the tube, the bulkhead contained a drawn-out section of tubing which served to contain a seed crystal for the beginning of each pass. Diphenyl ether is notorious for supercooling, and thus it became necessary to seed the molten zone at the start of each pass.

The bulkhead at the impure end of the tube carried glass tubes for filling the zone refiner tube, as well as for controlling the pressure within the larger zone refiner tube. The pressure was varied during the purification process. The ether was introduced as a liquid under atmospheric pressure. It was naturally saturated with air. When the zone refiner tube was full, it was evacuated to about 15 torr by a mechanical pump. After the outgassing had subsided somewhat freezing was initiated by touching the side of the tube with dry ice. This procedure usually brought on vigorous outgassing. Two passes of the heater were then made while the pump continued to evacuate the zone refiner tube. There was no noticeable outgassing on the second pass any time the zone refiner was run. After the second pass, the tube was pressurized with helium gas, to about one atmosphere, and then sealed off for the remainder of the refining. At least thirty passes were made before the diphenyl ether was removed.

The design of the zone refiner itself was also made by Mr. Roberts.

It will be briefly described, but his thesis should be consulted for full details.

Basically the zone refiner consisted of a plywood box 12 x 4 x 2 feet. This box was waterproofed so that it would contain water for extended periods of time. Each batch of diphenyl ether was in the zone refiner on the order of sixty days. The water was cooled to about 15°C by a mechanical refrigeration unit. Four of the tubes described above were mounted so that they were under the water except for the filling and evacuating tubes. A heater was contained in an aluminum box with rubber gaskets forming water tight seals with the zone refiner tubes. The entire heater assembly was driven down the length of the tubes by a worm drive mechanism. The rate of travel was 2.3 inches per hour. At the end of each pass the drive motor and the heater were automatically turned off. The heater box was manually returned to the starting end, and the whole process repeated.

After the required number of passes had been made the refiner tubes were removed from the zone refiner and the "good" diphenyl ether removed. The decision as to what part of the charge in the tube was good was based on the visual appearance of the crystalline ether. The refiner tubes were broken so that one section contained only good material. The diphenyl ether was removed from this section by melting in a "Chimney" where the zone refiner tube and its contents were heated by passing hot air around them. The diphenyl ether was collected and stored.

The final step in the purification of the diphenyl ether was undertaken when the calorimeter was complete. The ether was transferred

to a specially designed still (see Figure 10) which was connected to the "plumbing" of the calorimeter by a Swagelok fitting employing a Teflon ferrule to form the seal to the glass still. The still was evacuated along with the diphenyl ether chamber and the plumbing of the calorimater. The diphenyl ether was subjected to several freeze thaw cycles under reduced pressure. The pressure was maintained in the range 0.10 to 0.05 torr. When outgassing stopped and the pressure in the system remained reasonably steady, the "pot" of the still was heated with a heat light, and the diphenyl ether distilled into the condenser portion of the still. From there it was transferred into the calorimeter proper by manipulation of the valves in the plumbing system. In the first attempt to fill the calorimeter with diphenyl ether it was found necessary to install the bypass. This in turn made it necessary to start the process of filling the calorimeter all over again. The first time that the calorimeter was filled with diphenyl ether was condensed with dry ice applied to the outside of the condenser. However, during the second filling the condenser was air cooled. This seemed to work as well as using dry ice, and gave the added advantage that the diphenyl ether remained liquid, making it much easier to control in the filling operation.

During the filling operation a sight gauge was connected to the upper outlet of the diphenyl ether chamber. This gauge was in turn connected to the vacuum system. The distillation of diphenyl ether was continued until the level of the liquid in the condenser of the still and in the sight tube were equal, with liquid showing in the sight gauge. The reaction vessel was maintained at about one millimeter pressure up to this point, in order to prevent air leaking through the joint between the

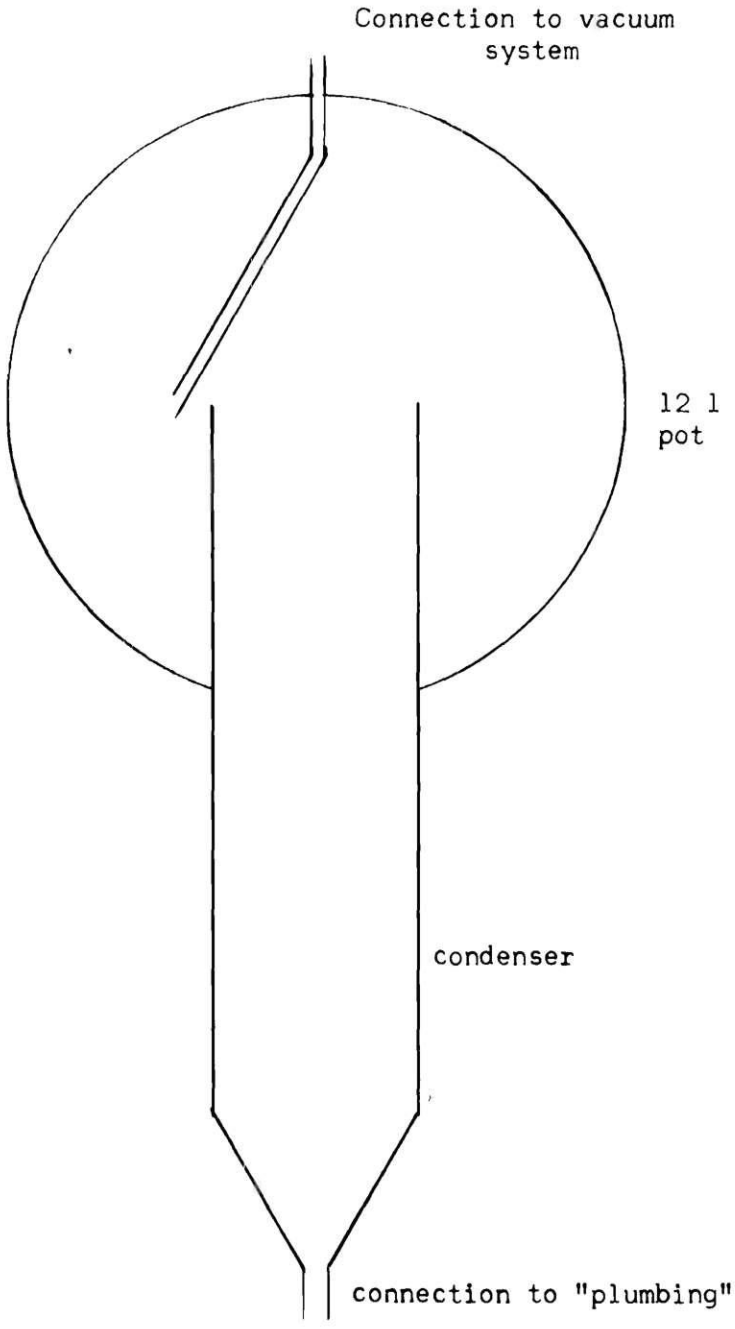

Figure 10. Vacuum Still for Diphenyl Ether.

finned cylinder and the support.

When it was felt that there was enough diphenyl ether in the condenser and in the calorimeter to fill the delivery system and still leave some over, the vacuum system was pressurized with helium to about atmospheric pressure. The reaction vessel was then cooled with ice so that a mantle would freeze. The cooling was carried on until no more change in liquid levels could be observed. The valve to the condenser was then closed, and those to the delivery system opened. The mantle was then thawed by putting hot water in the reaction vessel, thus forcing diphenyl ether out of the delivery system. This freezing of a mantle, and forcing diphenyl ether out the delivery system was repeated.

This completed the filling of the calorimeter. The sight tube was removed and the fitting where it had been mounted plugged with an aluminum plug. The same was done where the still had been mounted.

The final stage in purification of the diphenyl ether and the filling of the calorimeter diphenyl ether chamber were accomplished at the same time.

APPENDIX E

PREPARATION OF KNO_2

Since the subject of this investigation is the heat of dilution of potassium nitrite, it is obvious that KNO_2 in a high state of purity would be needed. Considerably less obvious was the way to obtain this pure KNO_2. The ACS[17] specifications for reagent grade call for a minimum assay of 94% KNO_2. Certainly this level of purity would not be acceptable for precise calorimetric work.

Part of the reason for the ACS specification may be found in earlier work. Oswald[18] discussed the purification of $NaNO_2$ by recrystallization. He prepared KNO_2 by reaction between $AgNO_2$ and KCl. The melting point reported by Oswald is 297.5°C. Other reported melting points for KNO_2 of various claimed purity range from 387°C,[19] to 441°C.[20]

This range in melting point emphasizes the range of purity in the samples used. Naturally, each worker had made his best attempts to purify the KNO_2 by one means or another.

In the work reported in this thesis, a number of methods of purification of KNO_2 were tried, but the method finally settled on was to prepare KNO_2 from $Ba(NO_2)_2$ and K_2CO_3. These illustrate the two possible routes to pure materials, purification of relative crude starting material or synthesis from pure starting materials.

For historical purposes some of the methods of purification will be discussed, along with the reason for discarding these methods.

Ray[21] has shown that it is possible to produce pure KNO_2 by passing impure KNO_2 through a column of IRA-400 in the NO_2^- form. This was tried on a large scale -- using five pounds of resin -- but the resulting KNO_2 was never free of traces of Cl^-. The method was abandoned for this reason, although it was later discovered in talks with Dr. H. A. Flashka that the source of the chloride ion was probably the distilled water used to prepare the solutions.

Zone refining, or Zone melting was also tried. Although a certain degree of purification was found after forty passes, it is doubtful that this purification was achieved by the zone refining. It is more probable that the purification was due to the reaction:

$$KNO_3 = KNO_2 + 1/2\ O_2$$

Zone refining was abandoned because the degree of purity achieved was not great enough, and because it would have required an inordinate amount of time.

Another high-temperature metnod that was tried was distillation of KNO_2 under reduced pressure. The mechanics of heating, of collecting the product, and of maintaining the desired pressure (0.1 torr) proved to be too demanding for this method to even yield enough KNO_2 to analyze. Obviously, it would not be suitable for preparing the needed quantity of KNO_2.

The high-temperature methods were abandoned at this point, but some speculation showed that a low temperature recrystallization might be successful. The rational was as follows. At room temperature it is impossible to separate out the last traces of nitrate (4 - 7%) or chloride

(1 - 2%) from KNO_2 by recrystallization from water. This observation has been made by Oswald (op. cit.) and studied by Ray.[21] It is to be noted that a similar difficulty is not observed with $NaNO_2$. Thus, it is necessary to explain the difference between $NaNO_2$ and KNO_2 as well as to explain why NO_3^- and Cl^- are incorporated in the KNO_2 lattice. One outstanding difference between $NaNO_2$ and KNO_2 is the fact that $NaNO_2$ undergoes a transition in the range 163° - 178°C,[22] while it has been reported that KNO_2 undergoes a transition at about -18°C.[23] Chang[24] reports a transformation of 250 ± 20 cal/mole at -17.7°C. The $NaNO_2$ transition has been studied by several methods. Kay et al.[22] find that above the transition temperature the nitrite ions are in a disordered structure (at 185°C) whereas they are ordered at 20°C. The nature of this disorder could not be determined from the neutron diffraction study of Kay et al.

If two assumptions are made regarding the KNO_2 transition at -18°C, it becomes possible to explain the incorporation of nitrate ions in the potassium nitrite lattice. These assumptions are 1. that the nitrite ions in KNO_2 change from an ordered structure below -18° to a disordered structure above -18° and 2. that the nature of this disorder is a rotation of the nitrite ion in a plane (or possible free rotation in three dimensions). The first of these assumptions is supported by the analogy with the $NaNO_2$ case. The lowering of the transition temperature would be expected on the basis of looser binding between the potassium ions and nitrite ions than between the sodium ions and nitrite ions due to the larger size of the potassium ion.

It is not as easy to justify the second assumption except by the

argument that the observed facts support this assumption. The N - O distance in the nitrite ion in $NaNO_2$ is 1.24 Å, while that in the nitrate ion is 1.23 Å. The dimensions of the nitrite ion in KNO_2 can not be given as they have not been determined with the precision with which the $NaNO_2$ dimensions are known. Ziegler[25] reported the results of an X-ray investigation of the structure of KNO_2, but because of equipment limitations, his answers reflected large uncertainties. Chang[24] also investigated the structure of KNO_2 by X-ray techniques. However, he was not able to locate the oxygen atoms except in a statistical way. That is he found that there were six possible sites for the oxygen atoms around each nitrogen atom, but that there are only two atoms of oxygen. Chang's results are also in question since he apparently did not make any effort to prepare pure KNO_2 for his experiments.

If one accepts the assumption that the nitrite ion is in a rotating state in KNO_2 at room temperature, then it is easy to understand how a nitrate ion can be substituted for a nitrite ion in the formation of the crystal lattice during recrystallization.

Having accepted these assumptions, it is an easy step to assume that if recrystallization could be conducted at temperatures below the transition (-18°C) temperature, then it should be possible to exclude nitrate ions from the lattice. The phase diagram of the system KNO_2 - H_2O as determined by Bureau[26] showed that it might be possible to recrystallize KNO_2 from an aqueous solution in the temperature range of -18° to -40°C. Experiments were undertaken to see if this were possible, and it did indeed prove possible to achieve separation between KNO_2 and small amounts of nitrate. However, the results are not clear cut since the crystal form

actually recovered was $KNO_2 \cdot 1/2\ H_2O$. Thus any arguments about the rotator state of the nitrite ion in KNO_2 at room temperature will have to be settled by some other means.

Despite the fact that pure KNO_2 was prepared by low temperature recrystallization, this method was abandoned as the yield was too small, both on a relative and absolute basis. Recrystallization was also carried out using methanol as a solvent and working in the range -20°C to dry ice temperature. Once again separation was achieved, but the yields were not large enough to make the method practical.

The method of preparing KNO_2 that was finally adopted consisted of reacting K_2CO_3 with $Ba_2(NO_2)_2$ in solution. The $Ba(NO_2)_2$ was prepared from $NaNO_2$ and $BaCl_2$ according the method of Witt and Ludwig.[27]

$Ba(NO_2)_2$ was chosen for an intermediate because of the relative insolubility of $Ba(NO_3)_2$. It was also attractive because of the larger temperature coefficient of solubility which it exhibits. This combination allowed for the purification of $Ba(NO_2)_2$ by repeated crystallization to remove the Cl^- introduced by using $BaCl_2$. If it had proved impossible to eliminate the final traces of chloride by recrystallization, it would have been a simple matter to remove chloride by "titration" with $AgNO_2$ or even $AgNO_3$. Any nitrate formed by decomposition of the silver salt would have been removed as $Ba(NO_3)_2$. However it was found that after two recrystallizations the chloride concentration was less than 0.1% of the anion concentration. Thus treatment with silver ions was unnecessary.

The "double decomposition" of $NaNO_2$ and $BaCl_2$ proceeded cleanly. A solution containing an excess of $NaNO_2$ was heated to boiling and a mixture of $BaCl_2$ and $NaNO_2$ as solids was added. The molar ratio was that

required by the reaction:

$$BaCl_2 + 2\ NaNO_2 = Ba(NO_2)_2 + 2\ NaCl \downarrow$$

The excess of $NaNO_2$ in the starting solution ensured complete conversion of the $BaCl_2$. The resulting slurry was heated for an hour at the boiling point. NaCl was filtered off while the mixture was still hot, and the resulting clear solution allowed to slowly cool to room temperature. Finally the mixture was cooled to near the ice point and the product, $Ba(NO_2)_2$, separated by filtration. This separation was clean as the temperature coefficient of solubility of NaCl is practically zero, while that of $Ba(NO_2)_2$ is large. Thus essentially no NaCl crystallized out during the cooling of the solution. As mentioned earlier, two recrystallizations were sufficient to lower the chloride concentration below the limit of detection.

After the $Ba(NO_2)_2$ had been prepared it was dissolved and reacted with a solution of K_2CO_3. Actually the reaction was carried out in the manner of a titration, adding K_2CO_3 to the $Ba(NO_2)_2$ solution until the pH of the mixture rose above pH 10. The $BaCO_3$ was removed by filtration, and the KNO_2 solution concentrated. The KNO_2 was recrystallized once to insure that no barium or carbonate ions were carried over into the final product. The resulting KNO_2 was air dried on the filter, and stored. No attempt was made to completely dry the product.

As the potassium nitrite product was not dry, no attempt was made to analyze the solid material. Instead analyses were made on a solution of KNO_2. Analysis for potassium ions was made by a procedure based on "Procedure No. 2" of Flaschka and Barnard.[28] Their method had to be

modified because the nitrite ion reacted with the tetraphenylboron. The modification consisted of destroying the nitrite ion by heating the sample in a solution of oxalic acid before adding the tetraphenylboron. Ten determinations of the K^+ concentration in the solution called "1 M" gave the concentration as 1.137 molal with a standard deviation of 0.016. The rather large standard deviation was due to the size sample which could be conveniently precipitated. The weight of the final precipitate was in the order of 0.1 gram with all weighings made on a Mettler H balance. The precision of this type of balance is reported to be 0.1 mg, but in this particular instance the mounting of the balance was such that its precision was closer to 1 mg.

The nitrite ion concentration in the "1 M" solution was determined by titration with Ce^{+4}. Since NO_2^- is unstable in acid solution, and Ce^{+4} insoluble in basic solutions, the following procedure was developed. The sample of NO_2^- was added to an excess of acidified Ce^{+4} with vigorous stirring. The excess Ce^{+4} was back titrated with As^{+3} in the presence of osmium tetroxide as a catalyst, as recommended by Kolthoff and Sandell.[29] Solutions of Ce^{+4} and arsenious acid were made up according to the instructions in Kolthoff and Sandell,[29] with the Ce^{+4} standardized against oxalic acid. Eight analyses gave the concentration as 1.1383 with a standard deviation of 0.0012. There is no statistically significant difference, at the 95% confidence level, between the concentration of K^+ ions and NO_2^- ions in the "1 M solution."

As the K^+ analysis using tetra-phenylboron was not very precise, and was also time consuming, it was discarded in favor of the titration of the nitrite ion as the routine analysis of solutions.

Results of the various analyses on the "1 M" solution are given in the Tables 2 and 3.

Table 2. Potassium Analysis on "1 M" Solution of KNO_2

Run No.	Concentration (molal)	
1	1.1147	
2	1.1071	$\bar{X}$ = 1.137 M
3	1.1313	
4	1.1338	σ = 0.016
5	1.1402	
6	1.1402	
7	1.1415	
8	1.1568	
9	1.1556	
10	1.1466	

Table 3. Nitrite Analysis on "1 M" Solution of KNO_2

Run No.	Concentration (molal)	
1	1.1388	
2	1.1376	$\bar{X}$ = 1.1383
3	1.1376	
4	1.1363	σ = 0.0012
5	1.1401	
6	1.1380	
7	1.1389	
8	1.1389	

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*Abbreviations used above follow the form given in Chemical Abstracts List of Periodicals.

VITA

Fielding Ficklen Harper was born on October 4, 1932, at Jabalpur, M. P., India.

He received an AB from Emory University in 1954.

He is married to the former Carol Hagebusch. They have three children, Kay, Stephen, and Sandra.